



**JOHN F. KENNEDY
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(Interim Report)

**CORROSION STUDY OF BARE AND COATED
STAINLESS STEEL**

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APPROVAL

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**CORROSION STUDY OF BARE AND COATED
STAINLESS STEEL**

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ABSTRACT

This report covers the work accomplished from February 1968, to date on a program, conducted for the Mechanical Design Division by the Materials Testing Branch, to evaluate the performance of austenitic stainless steel alloys used in fluid systems lines at KSC. Need for the program was dictated by the occurrence of numerous failures of stainless steel hardware, caused by pitting and stress-corrosion cracking, over the past several years. Tests have been conducted to determine the inherent corrosion susceptibility of several alloys - AISI Types 304, 304L, 316, 316L, 321 and 347 - and to evaluate the effectiveness of certain sacrificial-type protective coatings in preventing corrosion failures. The test samples, both unprotected and coated, have primarily been tubing sections and tubing assemblies employing 37°-flare fittings. Samples were placed in racks approximately 100 yards above high-tide line at Cape Kennedy. The racks were designed to provide complete exposure of half of each tubing sample and shelter from direct rain impingements of the other half. Protective coatings and treatments evaluated include organic- and inorganic-base zinc-rich paints, an aluminum-filled proprietary coating, and periodic surface treatment with a phosphoric acid wash.

General conclusions reached at this point in the program are as follows:

1. All of the unprotected tubing samples, regardless of alloy type, showed evidence of pitting initiation after about two-weeks exposure at the beach test site.
2. Samples of Types 321 and 347 appear to develop a larger pit population than the other alloys.
3. The deepest pit penetration (about 65% of the wall thickness) that has been discovered in the bare samples examined to date has occurred in Type 316 tubing. However, it is probable that actual pitting rate is independent of alloy type and that no one of the alloys evaluated has appreciably better resistance to pit penetration than the others.
4. The deepest pitting generally occurred in the sheltered portion of the tubing samples, probably because of the retention of deposits from salt fogs.
5. Zinc-rich coatings, both inorganic-base and organic-base, and an aluminum-filled coating, have afforded sacrificial protection to the stainless steels against pitting, for as long as 28 months, and against stress-corrosion cracking of fittings, for as long as 12 months. It is believed that a much longer effective coating life can be expected.

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1.0 INTRODUCTION

- 1.1 This is an interim report of the work performed (from February, 1968 to date) on a program to evaluate the performance of various types of stainless steels for use in fluid systems at Kennedy Space Center (KSC), and was conducted by the Materials Testing Branch (SO-LAB-41 for the Mechanical Design Division (DD-MDD) of the Design Engineering Directorate (DE) at KSC.

Numerous tubing lines are used in Ground Support Equipment (GSE) fluid systems, such as the high-pressure gas supply lines and propellant loading systems. The high-pressure systems generally utilize small diameter tubing connected with 37°-flare fittings (AN, MS, or KC). The vacuum-jacketed cryogenic propellant lines utilize thin-walled bellows sections, for the flexibility needed for thermally generated dimensional changes, and general movement of the lines.

- 1.2 The austenitic stainless steels, with their unusual combination of attractive mechanical and chemical properties, are the preferred materials for these applications. These properties include relatively high strength, exceptional toughness (even at low temperatures), good fabricability (bending, flaring, welding), and excellent general resistance to many corrosives, including the hypergolic propellants used at KSC. This latter property derives largely from the presence of a protective surface film (a complex oxide of iron, chromium, and nickel), which tends to form spontaneously on the stainless steels in the presence of sufficient oxygen.
- 1.3 However, this characteristic passive surface film that contributes so effectively toward general corrosion resistance produces in the stainless steels a susceptibility to pitting (a severe, localized form of corrosion). Pitting, which is also a characteristic of aluminum alloys, occurs from electrolytic action at small breaks in the passive film whenever there is moisture present on the surface of the metal. In a warm, humid, seacoast environment, such as the KSC area, the factors of condensed moisture, salt, and relatively high ambient temperatures combine to produce extremely corrosive conditions.
- 1.4 Another specialized form of corrosion failure occurring in stainless steels, exposed to this same environment, is stress corrosion cracking. Highly stressed parts (such as B-nuts and sleeves, used in tubing fittings) are particularly susceptible to this failure mode, which results from the interaction of the corrosive environment and the mechanical stresses,
- 1.5 The mechanisms of the corrosion processes, as they affect the performance of the austenitic stainless steels in the KSC area, will be discussed more fully in a subsequent paragraph of this report. The relevance of the corrosion processes to the performance of stainless steel hardware at KSC is well documented in a listing of failure analysis reports (presented in Appendix A).

The listing (covering a period of approximately four years) has been divided into two sections; one containing failures attributable to pitting corrosion, and the other section containing failures attributable to stress corrosion cracking. All of these failures occurred in austenitic stainless steel tubing (hardlines), bellows expansion sections, or tubing fittings. Although this listing is essentially complete with regard to failure analyses performed on this hardware, it is not nearly complete with regard to the total number of failures (or incipient failures) that have occurred with this hardware at KSC during the past four years. Many incipient failures were "prevented" by the routine replacement of severely corroded, but not completely perforated, stainless steel tubing lines. Numerous failures that occurred were not submitted to the Malfunction Analysis Branch (SO-LAB-2) for analysis, because of the nature of the tubing failure was evident to the cognizant personnel.

- 1.6 Typical examples of the perforation of stainless steel tubing as a result of pitting corrosion, and of stress-corrosion failure are illustrated in Figures 1, 2, and 3.

Figure 1 shows an enlarged view of the surface of a 3/8-inch diameter tube with the perforation indicated by an arrow (View A). A cross-section through the tubing wall in the perforation area is also shown (View B) enlarged to 50X. This failure occurred in a high-pressure line on the Astronauts' Transfer Van.

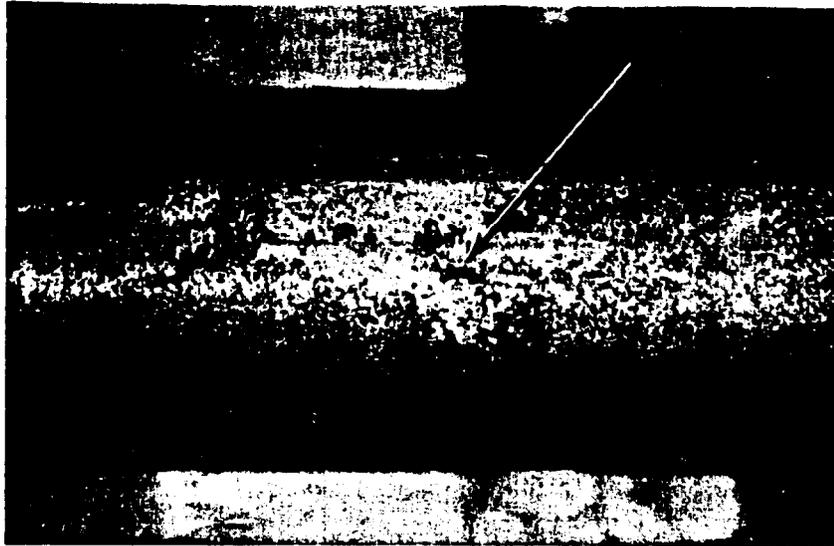
Figure 2 similarly shows the surface and cross-section in the perforated area of a section of stainless steel tubing, that was used in a gaseous hydrogen line at Complex 34. Note the ring of corrosion product on the tube surface around the perforated point in View A. A magnification of 18X is shown in View B.

Figure 3 illustrates a typical example of stress-corrosion failure. The sample shown is a stainless steel B-nut sleeve containing a longitudinal crack extending the full length of the sleeve. This sample had been removed from a console line used on a mobile-launcher service arm.

- 1.7 Control methods for the stainless steel corrosion generally have considered two factors: basic susceptibility of the various grades of austenitic stainless steels to pitting corrosion (or to stress corrosion cracking), and surface treatments or coatings to prevent or delay access of the environment to the stainless steel. With regard to the former, it appeared to be the general consensus, at the time this program was initiated, that Type 316 stainless steel was significantly more resistant to pitting corrosion than most of the other grades, and particularly more resistant than Type 304. This conviction is probably reflected in specification MSFC-SPEC-10M01734,

which specifies Type 316 (stainless steel) for tubing applications. Exposure tests of the type conducted by the International Nickel Company (and others) at Kure Beach, North Carolina tend to justify this conviction. However, it should be recognized that these tests have usually employed flat panel samples, exposed near the beach in "standard" ASTM (American Society for Testing Method) racks, with the samples at 30" or 45" to the horizontal, and completely exposed (uncovered) to the elements. Evaluation of the corrosion resistance is based on weight loss as a function of exposure time. Whereas the tests results so obtained are certainly valid for the conditions of exposure, it was believed that these test conditions did not adequately represent the service environment at KSC, nor was the method of evaluation of corrosion resistance believed to be valid for the applications at KSC. For example, on the service structures, various "degrees" of exposure are experienced. Some runs of tubing are completely exposed to the elements, whereas, others are sheltered from direct rain impingement but are exposed to the salt fog intrusions. When pitting corrosion is active on a pneumatic line (for example), the line has failed when a single leak occurs. Therefore, evaluation of the extent of corrosion by total loss of weight would hardly be relevant for most tubing applications. With regard to anti-corrosion surface treatments and coatings, some practices have been used by stage and maintenance contractors at KSC. McDonnell-Douglas has used a three-coat system to protect stainless steel tubing, with some success in extending useful life. This system consists of a resin-acid wash primer, a zinc-chromate primer, and an epoxy top coat. Other contractors applied a cleaning program that utilizes a solution specified in standard MIL-M-10578, Type II (a phosphoric acid wash that is periodically used a "wipe-on, wipe-off" cleaner).

- 1.8 The experimental program reported herein was designed to investigate both of these factors: inherent corrosion susceptibility, and use of protective treatments and coatings. Comparative exposure tests were to be conducted with bare (unprotected) samples of the particular grades of austenitic stainless steels likely to be applied at KSC. These include Types 304, 316, 321, 347, **304L**, and 316L. Surface treatment methods and anti-corrosion coatings were also to be evaluated by exposure tests. The emphasis in this part of the program was specifically directed to coatings that could afford sacrificial protection to the stainless steel substrate, since it is inevitable that some mechanical damage to the coatings will occur in service. The zinc-rich paints, some of which have been used to protect the large GSE structures at KSC, are examples of sacrificial coatings. A prime consideration of the exposure tests was that both hardware and exposure conditions must be representative of the KSC service applications.
- 1.9 Throughout the program, close liaison between the Materials Testing Branch and the Design Directorate's representative (Mr. M. G. Olsen, DD-M **DD-1**), was maintained.



VIEW A

Magnification: 5X

Perforation on tube surface indicated



0.035"
Tubing
Wall

VIEW B

Magnification: 50X

Cross-section through perforation in tubing wall

Figure 1. Perforation of Stainless Steel Tubing Used in High-Pressure Oxygen System on Astronauts' Transfer Van



Magnification: 4X

Sleeve full-length stress corrosion crack

Figure 3. Cracked B-Nut Sleeve From Control Console Line,
Mobile Launcher Service Arm 8, Complex 39

2.0 MATERIALS AND PROCEDURES

- 2.1 The first phase of the program was devoted to a survey and assessment of recent technical literature in the areas of mechanisms of corrosion of stainless steels, exposure testing in seacoast environments, and the use of protective coatings for stainless steel.

This survey was completed in June' 1968, and a separate report of the results was submitted to the requester at that time (also included herein, refer to Appendix B).

- 2.2 The major stainless steel test materials consisted of tubing Types 304, **304L**, 316, **316L**, 321, and 347. A single tubing size (**0.375"** outside diameter, 0.035" wall thickness) was used throughout the program in the types (grades) listed. Samples were obtained from KSC stocks when available. One sample (10-foot length) of Type 316, meeting specification **MSFC-SPEC-10M01734**, was obtained by the requester and submitted for inclusion in the testing program. This sample was 0.375" in diameter, with a thickness of 0.049' .

Samples of the major testing materials were submitted to the Malfunction Analysis Branch Support Laboratory for chemical analysis. A listing of these materials, their sources, and chemical compositions is presented in Table 1. Also indicated (Table 1) is an additional grade of Type 304 tubing, **1/8-hard** condition, meeting specification MI L-T-6845. This additional material was included to evaluate the effects of the corrosive environment on stainless steel in a partially cold worked condition. Additionally, several samples of Type **304L** supply lines, removed from the Service Structure at Complex 34 (because of deterioration due to pitting corrosion), were also obtained by the requester for testing.

- 2.3 Metallurgical analyses (of the as-received condition) were performed with samples of the seven test materials listed in Table 1 to determine their content of non-metallic inclusions, grain size, and susceptibility to **intergranular** corrosion. Sections of each tubing material were mounted, ground, and polished metallographically for microscopic examinations. Each sample was examined at 100X for type and number of non-metallic inclusions, in accordance with ASTM E-45, Method A. The samples were then electrolytically etched in 10% ammonium persulphate and examined microscopically at 100X. The grain size of each material was rated according to Plate II, ASTM E-112. A **1 1/2-inch** length of each tubing material was placed in a flask containing 10% copper sulphate in **10%** sulfuric acid. The **solutions** were maintained at boiling for 48 hours, with evaporation being **prevented** by the use of **ref lux** condensers attached to the flasks. Following exposure to the boiling solution, each sample was flattened between the platens of a compressive loading machine to a separation of 0.140 " (four times the tubing wall thickness). The severely deformed areas of each sample were examined with a low-power microscope for evidence of cracking.

Table 1. Identification of Major Sample Materials

Alloy Type	Condition	Applicable Specification	Source	Chemical Composition, Percent of Elements						Remarks
				Carbon	Manganese	S i l i c o n	Sulfur	Chromium	Nickel	
304	Annealed	MIL-T-8504	KSC Stocks	0.057	1.20	0.71	0.017	17.98	9.20	-
304	1/8-hard	MIL-T-6845	KSC Stocks	0.049	1.81	0.77	0.009	17.51	9.77	-
304L	Annealed	ASTM-A269	Direct purchase, vendor	0.030	1.81	0.66	0.010	18.58	9.97	-
316	Annealed	ASTM-A269	KSC Stocks	0.059	1.87	0.41	0.016	16.73	12.00	Note1
∞ 316L	Annealed	ASTM-A269	Direct purchase, vendor	0.025	2.10	0.44	0.015	16.71	12.50	Note 2
321	Annealed	MIL-T-86066	KSC Stocks	0.047	1.65	0.68	0.010	17.42	10.97	Note3
347	Annealed	ASTM-A269	Direct purchase vendor	0.065	1.79	0.73	0.005	19.96	10.64	Note4

Note 1 - Molybdenum 2.19

Note 2 - Molybdenum 2.30

Note 3 - Titanium 0.42

Note 4 - Niobium 0.28

- 2.4 The basic exposure test specimens consisted of five-foot lengths of tubing, mounted horizontally in a support rack. The tube ends were closed with plastic caps (Caplugs) to prevent introduction of corrodents to the inner surfaces. For special tests involving internally pressurized samples, several five-foot sections of Types 304, 304 1/8-hard, and 316 were prepared with flared ends for the attachment of AN fittings.

Several smaller tubing assemblies, consisting of Type 304, back-to-backs, approximately 12 inches long, were prepared with various flare fittings attached. The samples were used in the evaluation of protective coatings at tubing junction areas.

- 2.5 The coatings evaluated consisted mainly of zinc-rich paints, and a special proprietary aluminum-filled material. A single vendor's material was selected for testing each category of the coatings, since it was the purpose here to evaluate types of materials (rather than to qualify many materials of a given type). The following coating materials were applied:

Koppers Organic Zinc Paint
Carbo Zinc-11 Inorganic Zinc Paint (Carboline Company)
O139-AR-3 (Zinc Modified)
O 139-AR-7 (Goodrich)

The latter two materials (AR-3 and AR-71 are proprietary coating materials, not yet commercially marketed, containing aluminum powder. Their concept was developed by the KSC Materials Testing Branch (MTB), and the test materials were formulated by Goodrich. MTB modified the AR-3 by the addition of zinc powder. The AR-7 was applied to the samples without modification of the coating.

A self-sealing polyethylene tape was also evaluated, to a limited extent, being applied to some tubing assemblies with attached fittings.

- 2.6 The standard surface preparation for the tubing samples, prior to the application of the organic-base coatings, consisted of solvent cleaning with acetone followed by phosphoric acid wash (specification MIL-M-10578, Type II). Surface preparation for application of the inorganic-base zinc-rich paint consisted of abrasive blasting with 20/30-mesh silica sand.

Passivation with 20% nitric acid or 20% nitric acid with 2% sodium dichromate was applied to several tubes that were then exposed without further treatment.

One sample of Type 304 tubing, that had been electropolished, was submitted for testing by the requester.

- 2.7 Application of the zinc-rich coatings was effected by conventional spray equipment, in accordance with the manufacturer's recommendations. The same general application procedure was used for the aluminum-rich material, the 0139-AR-7 containing 40Wt. % Al powder, and the zinc modified coating (0139-AR-3 Zn, containing 30 Wt. % Al powder and 40 Wt. % Zn powder). All these coatings were applied to a nominal dry film thickness of 4 mils. Coating thickness was determined by measuring with a micrometer. On each of the coated samples, deliberate defects in the coatings were introduced by scribing Xs through them to the bare metal.

Organic zinc-rich paint was brush applied to several samples of the "used" material from Complex 34. Surface preparation of these samples, prior to application of the paint, consisted of solvent wiping only (direct application of paint after wiping lightly with an acetone-dipped cloth), and of solvent wiping followed by the phosphoric acid wash.

- 2.8 The test samples were installed in support racks, located on the beach near the tip of Cape Kennedy approximately 300 feet from the high-tide line. The racks provided for horizontal mounting of the samples with half the tube length sheltered from direct rain impingement by a cover. The other half of the tube length projected from the shelter and was completely exposed to the elements. One of the racks was adapted for internal pressurization of several tubing samples. These samples had one end closed with plugs, and the other end manifolded to a GN2 supply at nominally 2,000 psi. This internal pressure resulted in a hoop stress of about 10,000 psi. The racks were positioned at the test site such that the tube length was oriented in a north-south direction. An illustration of one such test rack, with tubing samples installed, is shown in Figure 4. The tubing samples were secured to the rack support bars by means of stainless steel Adel Clamps with polytetrafluoroethylene cushions.
- 2.9 Tubing samples were installed in Test Racks (No. 1, 3, and 4) at the test site, and a tabulation of the samples is presented in Table 2.
- 2.10 Evaluation of the exposure-test samples consisted of regular visual inspections of both the bare and coated samples. Periodically, photographs were made for documentation, and metallurgical analyses were performed on several samples (removed from the exposure racks). From the visual inspections, the first evidence of pitting initiation on the bare samples was noted, and adhesion and sacrificial protection on the coated samples were evaluated. After an exposure period of six to seven months, four tubing samples (No. 7, 8, 9, and 10 in Test Rack 3) were removed and brought to the laboratory for examination. Following the laboratory examination, the samples were returned to the beach test site for continued exposure. After a total exposure of approximately 28 months, these same samples, together with samples 4, 5, 6, and 37, were removed (from Test Rack 3) for complete metallurgical examination. Two tubing-assembly samples (34 and 37, from Test Rack 4) were removed for metallurgical analysis after an exposure

period of 12 to 14 months. One of these assemblies was bare, and the other had been sandblasted and coated with inorganic zinc paint. A comparative evaluation of these assemblies was performed. The tubing samples were photographed to show typical areas of pitting corrosion, and these areas were then examined extensively with a low-power microscope. The deeper pits were identified by this method of surface inspection. Portions of the sample tubes containing the deep pits were prepared metallographically for microscopic examination. The pit areas were polished as cross sections and were examined microscopically at intervals during the polishing process, so that the deepest penetration of the pits in the tubing wall was determined. Photomicrographs of the microsections were obtained to show pit depth.

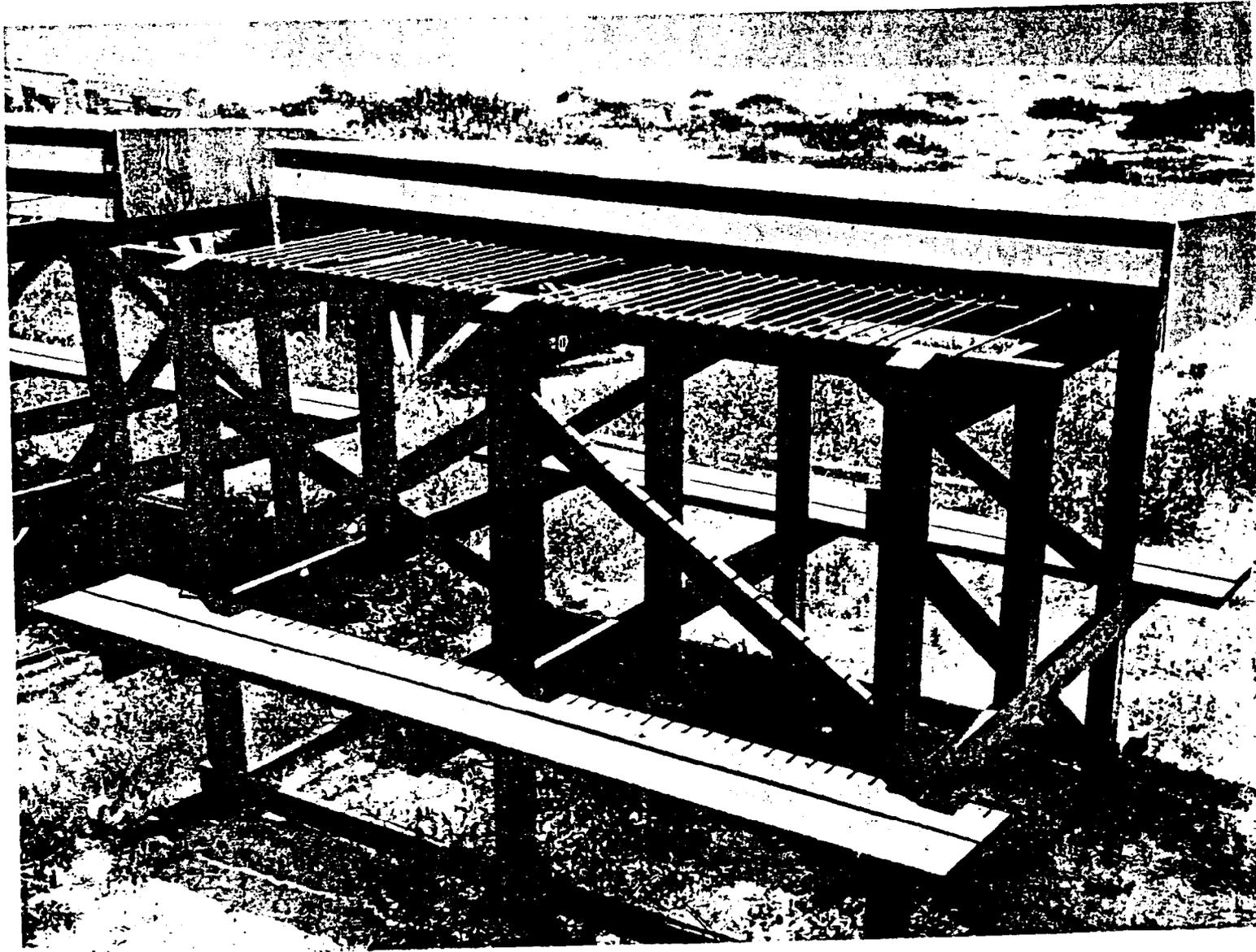


Figure 4. Corrosion Test Rack Number 3 With Tubing Samples at Cape Kennedy Beach Test Site

Table 2. Loy of Tubing Samples in Corrosion Test Racks

<u>TEST RACK NO. 3</u>				
<u>Sample Position</u>	<u>Alloy Type</u>	<u>Surface Preparation</u>	<u>Coating</u>	<u>Date Installed</u>
1	321	Passivated, 20% HNO ₃	None	May 20, 1968
2	304L	Passivated, 20% HNO ₃	None	May 20, 1968
3	304 1/8-hard	Passivated, 20% HNO ₃	None	May 20, 1968
4	316L	Solvent cleaned	None	April 22, 1968
5	304L	Solvent cleaned	None	April 22, 1968
6	347	Solvent cleaned	None	April 11, 1968
7	304 1/8-hard	Solvent cleaned	None	April 22, 1968
8	316	Solvent cleaned	None	April 11, 1968
9	321	Solvent cleaned	None	April 11, 1968
10	304	Solvent cleaned	None	April 11, 1968
11	304	Abrasive blasted	inorganic Zinc	April 25, 1968
12	304 L Removed from Complex 34	Solvent wiped, MIL-M-10578, Type II	Organic Zinc	April 30, 1968
13	304 L Removed from Complex 34	Solvent wiped, MIL-M-10578, Type II	Organic Zinc	April 30, 1968
14	304 L Removed from Complex 34	Solvent wiped, MIL-M-10578, Type II	Organic Zinc	April 30, 1968
15	304 L Removed from Complex 34	Solvent wiped, MIL-M-10578, Type II	Organic Zinc	April 30, 1968
16	316L	Solvent cleaned	None	April 22, 1968
17	304L	Solvent cleaned	None	April 22, 1968
18	347	Solvent cleaned	None	April 11, 1968
19	304 1/8-hard	Solvent cleaned	None	April 22, 1968
20	316	Solvent cleaned	None	April 11, 1968
21	321	Solvent cleaned	None	April 11, 1968
22	304	Solvent cleaned	None	April 11, 1968
23	304	Abrasive blasted	Inorganic Zinc	April 25, 1968

Table 2. Log of Tubing Samples in Corrosion Test Racks (Continued)

TEST RACK NO. 3 (Continued)

<u>Sample Position</u>	<u>Alloy Type</u>	<u>Surface Preparation</u>	<u>Coating</u>	<u>Date Installed</u>
24	316	Passivated, 20% HN03	None	May 20, 1968
25	347	Passivated, 20% HN03	None	May 20, 1968
26	316L	Passivated, 20% HN03	None	May 20, 1968
27	304	Passivated, 20% HN03	N o n e	May 20, 1968
28	316	MIL-M-10578 (6 month intervals)	None	April 25, 1968
29	304	MIL-M-10578 (6 month intervals)	None	April 25, 1968
30	304	MIL-M-10578 (1 month intervals)	None	April 25, 1968
31	304	MIL-M-10578 (12 month intervals)	None	April 25, 1968
32	304	MIL-M-10578	Organic Zinc	April 25, 1968
33	304	MIL-M-10578	Organic Zinc	April 25, 1968
34	304	MIL-M-10578	Organic Zinc	April 25, 1968
35	304	MIL-M-10578	Organic Zinc	April 25, 1968
36	316 (MSFC 10M01734)	MIL-M-15078	None	April 25, 1968
37	316 (MSFC 10M01734)	Solvent cleaned	None	April 25, 1968

TEST RACK NO. 4

4	304	Electropol ished	None
5	316	Passivated in 20% Nitric Acid - 2% Sodium Dichromate	None

Table 2. Log of Tubing Samples in Corrosion Test Racks (Continued)

<u>TEST RACK NO. 4 (Continued)</u>				
<u>Sample Position</u>	<u>Alloy Type</u>	<u>Surface Preparation</u>	<u>Coatina</u>	<u>Date Installed</u>
6	304	Passivated in 20% Nitric Acid - 2% Sodium Dichromate	None	
7	304	Passivated in 20% Nitric Acid - 2% Sodium Dichromate	None	
8	316	Passivated in 20% Nitric Acid - 2% Sodium Dichromate	None	
9	304	Abrasive blasted	Inorganic Zinc	14 August 1969
10	304	Abrasive blasted plus MIL-M-10578	Inorganic Zinc	14 August 1969
24	304	MIL-M-10578	Organic Zinc	23 January 1970
25	304	MIL-M-10578	Organic Zinc	23 January 1970
26	304	Abrasive blasted	Organic Zinc	23 January 1970
27	304	Abrasive blasted plus MIL-M-10578	Organic Zinc	23 January 1970
28	316	MIL-M-10578	Organic Zinc	23 January 1970
29	316	MIL-M-10578	Organic Zinc	23 January 1970
30	304	Solvent cleaned	0139-AR3-Zn	23 January 1970
31	304	Solvent cleaned	0139-AR7	23 January 1970
32	304	Solvent cleaned	0139-AR7	23 January 1970

Table 2. Log of Tubing Samples in Corrosion Test Racks (Continued)

TEST RACK NO, 4 (Continued)

<u>Sample Position</u>	<u>Alloy Type</u>	<u>S u r f a c e Preparation</u>	<u>Coating</u>	<u>Date Installed</u>
33*	304 Assembly	Solvent cleaned	None	17 July 1969
34*	304 Assembly	Solvent cleaned	None	17 July 1969
35*	304 Assembly	Abrasive blasted	Inorganic Zinc	14 August 1969
36*	304 Assembly	Abrasive blasted	Inorganic Zinc	14 August 1969
37*	304 Assembly	Abrasive blasted	Inorganic Zinc	14 August 1969
38*	304 Assembly	Solvent cleaned	None	9 September 1969
39*	304 Assembly	Solvent cleaned	LPS-1	9 September 1969
40*	304 Assembly	Solvent cleaned	LPS-3	2 March 1970
40**	304 Assembly	Solvent cleaned	LPS-3	2 March 1970

TEST RACK NO. 1

(All samples internally pressurized to 2000 psi)

26	304 1/8-hard	Solvent cleaned	None	24 October 1969
28	304 1/8-hard	Solvent cleaned	None	24 October 1969
30	316	Solvent cleaned	None	24 October 1969
32	316	Solvent cleaned	None	24 October 1969
34	304	Abrasive blasted	Inorganic Zinc	24 October 1969
36	304	Abrasive blasted	None	24 October 1969
38	304	Solvent cleaned	None	24 October 1969
40	304	Solvent cleaned	None	24 October 1969

*Sheltered portion of rack

**Exposed portion of rack

3 .0 RESULTS

3.1 Metallurgical Analyses of Initial Materials

This section contains the results of various tests performed on the tubing materials in the "as received" condition (described in paragraph 2.3).

3.1.1 Intergranular Embrittlement. Microscopic examination of the samples exposed to the boiling copper sulphate and then flattened revealed no evidence of surface cracking associated with intergranular attack in any of the test materials. Some very small surface cracks, not associated with grain boundaries, were detected in the Type 32 1 samples. It is believed that these surface defects were caused by localized attack of the copper sulphate solution at non-metallic inclusions in the Type 321 tubing surface.

3.1.2 Non-Metallic Inclusions. The results of the inclusion counts in terms of the frequency (number of fields) of each inclusion type, size, field rating, and the worst field of each type are listed in Table 3. These ratings indicate the sample materials to be of normal "cleanliness" for air-melted stainless steels. The oxide content of Types 321 and 347 was considerably higher than that of the other materials, and this probably results from oxidation of some of the reactive-metal additives (titanium, niobium, and tantalum) used for carbide stabilization in these grades.

3.1.3 Grain Size. The results of the grain size determinations are presented in Table 4. All of the test materials had a grain size of 7 or smaller, except Type 304L, which was rated 6 1/2. Size 7 or smaller is considered desirable in stainless steel tubing materials.

3.2 Visual Inspection of Exposure Samples

3.2.1 Visual inspections of the samples were made at frequent intervals, particularly in the early stages of the exposure tests. It was found that all of the bare tubing samples, solvent cleaned (only) prior to exposure, developed corrosion sites within 11 days of exposure.

The sample of Type 304 that had been electropolished (Rack Number 4, Sample 4) showed corrosion initiation after 21 days of exposure. Corrosion initiated on the passivated samples (Rack Number 4, Samples 5 through 8) after 30 days of exposure. Periodic cleaning with the phosphoric acid wash (MIL-M-10578, Type II) was apparently beneficial if applied at monthly intervals, at least on the basis of superficial inspection. Closer inspection with a hand lens revealed that extensive pitting had occurred on the cleaned sample, and suggested that the main benefit was cosmetic (removal of corrosion products that otherwise tended to collect on the less frequently cleaned (or not cleaned) sample).

Table 3. Inclusion Counts of Tubing Materials

Material	Field Rating	Type and Frequency					
		TYPE A		TYPE B		TYPE D	
		Thin	Heavy	Thin	Heavy	Thin	Heavy
304	1	3	1*	14	1	6	5
	1 1/2	4*	0	9	1	15	11
	2	0	0	6*	3*	8*	11*
304 1/8-Hard	1	14	0			15	1*
	1 1/2	6*	0	22	0	12	0
	2	0	0	3*	0	2*	0
304L	1	3	0	4	0	8	2*
	1 1/2	2*	0	23	0	7	0
	2	0	0	15	0	1*	0
	2 1/2	0	0	1"	0	0	0
316	1	3*	1*	12	0	11	9
	1 1/2	0	0	30	3	22	5
	2	0	0	16	5*	15*	6
	2 1/2	0	0	4*	0	0	1*
316L	1	2	2*	16	0	20	5
	1 1/2	1"	0	13	0	13	3
	2	0	0	18	2*	10"	7*
	2 1/2	0	0	1*	0	0	0
321	1			2	0	0	2
	1 1/2			14	2	4	0
	2			14	4	8	20
	2 1/2			10	1*	4*	8*
	3			6	0	0	0
	4			5*	0	0	0
347	1					8	8
	1 1/2			0	0	2	8
	2			20	10	12	8
	2 1/2			14	8*	2*	4
	3			6*	0	0	4*

* Denotes rating of worst field for each inclusion type and size

Table 4. Grain Size Determinations for Tubing Materials

<u>Material</u>	<u>ASTM Grain Size</u>
304	7
304 1/8- Hard	7
304L	6 1/2
316	8
316L	7
321	7 1/2
347	8

After approximately six months of exposure, there was a large accumulation of corrosion products on all of the bare samples, particularly on the sheltered half of each tubing sample. This accumulation continued, and at the present time, the sheltered sections are almost completely covered with the brownish corrosion products. Rain impingement on the exposed-tubing sections was fairly effective in removing the bulk of the corrosion products, and the main visible evidence was a brownish ring that encircled each active major pit. The bare tubing assemblies showed extensive deposits around the B-nuts and sleeves. All bare samples had extensive corrosion-product accumulations at the Adel clamps (used for securing the tubing samples to the racks).

3.2.2 The organic-base zinc-rich paint has been generally very effective in preventing corrosion of the stainless steels. In approximately 28 months of exposure, only one coated sample has shown any evidence of active corrosion. This occurred on one of the samples of Type **304L** removed after several years of service at Complex 34. The sample was coated with the organic zinc paint by brush application prior to exposure testing. The active corrosion occurred at the tubing interface in a brazed joint. Although small areas of flaking of the zinc paint have been noted on some of the other samples, there has been no evidence of active corrosion in these flaked areas. In fact, the organic zinc paint appears to afford sacrificial protection to bare areas of considerable extent. On several of the coated tubing samples, bare sections up to **2-inches** in length were deliberately left uncoated, and to date these areas are free from significant pitting. The inorganic-base zinc-rich paint, which was applied over a sandblasted surface, has adhered well to the tubes and the tubing assemblies, with no evidence of flaking. The sacrificial-protection effectiveness of the inorganic

zinc is also excellent. One tubing assembly was deliberately left with an uncoated strip (approximately 3/16" wide, and extending the entire length of the assembly). There has been no evidence of corrosion on this exposed, sandblasted stainless steel surface. The aluminum-rich and aluminum-zinc-rich proprietary coatings have adhered completely, and have evidently weathered well. No corrosion of the stainless steel substrate has occurred, and there is no evidence of deterioration of these coatings.

The general appearance of several of the coated and bare test specimens in Racks Number 3 and 4 is shown in Figures 5 through 11. Figures 5 and 6 show the underside of a group of bare and coated tubing samples in the sheltered section of Rack Number 3 after approximately three months exposure. The four coated samples in Figure 5 are the tubes removed from Complex 34 and brush coated with organic zinc paint. Two of the tubes also have short sections wrapped with self-sealing polyethylene tape. Note that three of the coated tubes have bare spots near the end caps. These bare spots have not shown active corrosion during the total exposure period of approximately 30 months; evidently because of sacrificial protection afforded by the zinc coating. The dark spots on the bare tubes are accumulations of corrosion products around active pits.

Similar conditions are shown on the bare samples illustrated in Figure 6. The single coated sample at the bottom of the photograph has the inorganic zinc paint applied over a sandblasted surface. This coating has remained intact after 30 months exposure.

Figures 7 and 8 show other bare and organic-zinc coated tubes in the exposed and sheltered sections, respectively, of Rack Number 3 after approximately 30 months exposure. The coating was applied to "new" tubing samples that had been cleaned with the phosphoric acid wash. These samples, including intentional bare areas (or tape wrapped areas), near the end caps, have remained essentially free of corrosion during this exposure period.

Figures 9 and 10 show coated tubing samples in exposed and sheltered sections of Rack Number 4 after 10 months of exposure. The three samples at the left side of Figure 9 were coated with the AR-7 (or zinc modified AR-31 material. The other six samples (shown in Figure 9) were coated with organic zinc paint, after various surface preparations. In Figure 10 (the sheltered portion of this same sample group), one of the AR-7 samples is not shown. The two samples at the left side (Figure 10) are the AR-7 and the zinc-modified AR-3 (the latter being the darker grey coating).

These coatings have remained entirely intact and protective to the stainless steel substrate during the 10 months of exposure. Slight flaking of the organic zinc paint has occurred on the sheltered side of two of the samples, at the X-shaped scribe marks in the coatings. However, the organic zinc coating has continued to protect the substrate in these areas.

Figure 11 shows two tubing assemblies removed from the sheltered section of Rack Number 4. The sample on the left side has been sandblasted and coated with inorganic zinc paint, and was exposed at the corrosion test site for 12 months. The bare sample was exposed for 14 months. The B-nuts and end plugs were removed, exposing the flared ends of both samples. The zinc coated sample showed no evidence of corrosion. The bare sample had undergone considerable crevice corrosion in the B-nut area, and there were large corrosion deposits under both the B-nut and sleeve. Several longitudinal cracks were noted in the sleeve. The extent of the stress-corrosion cracking, in this B-nut sleeve is described in more detail in subsequent paragraphs herein. It is evident that the zinc coating affords protection against crevice corrosion and stress-corrosion cracking in the area of tubing attachments.

- 3.2.3 The group of internally pressurized samples in Rack Number 1 have been exposed approximately 14 months. Only one of these samples was coated (inorganic zinc paint over a sandblasted surface), and it shows no evidence of corrosion or coating deterioration. The bare samples (Types 304, 304 1/8-hard, and 316) all show extensive pitting and a large accumulation of corrosion products on the sheltered halves, as did the unpressurized samples in an equivalent exposure period. No complete penetrations of any of the samples have occurred to date. The system is self-inspecting, since each sample is provided with a separate pressure gage. Perforation of the tubing wall by pitting will be indicated by a loss of pressure.

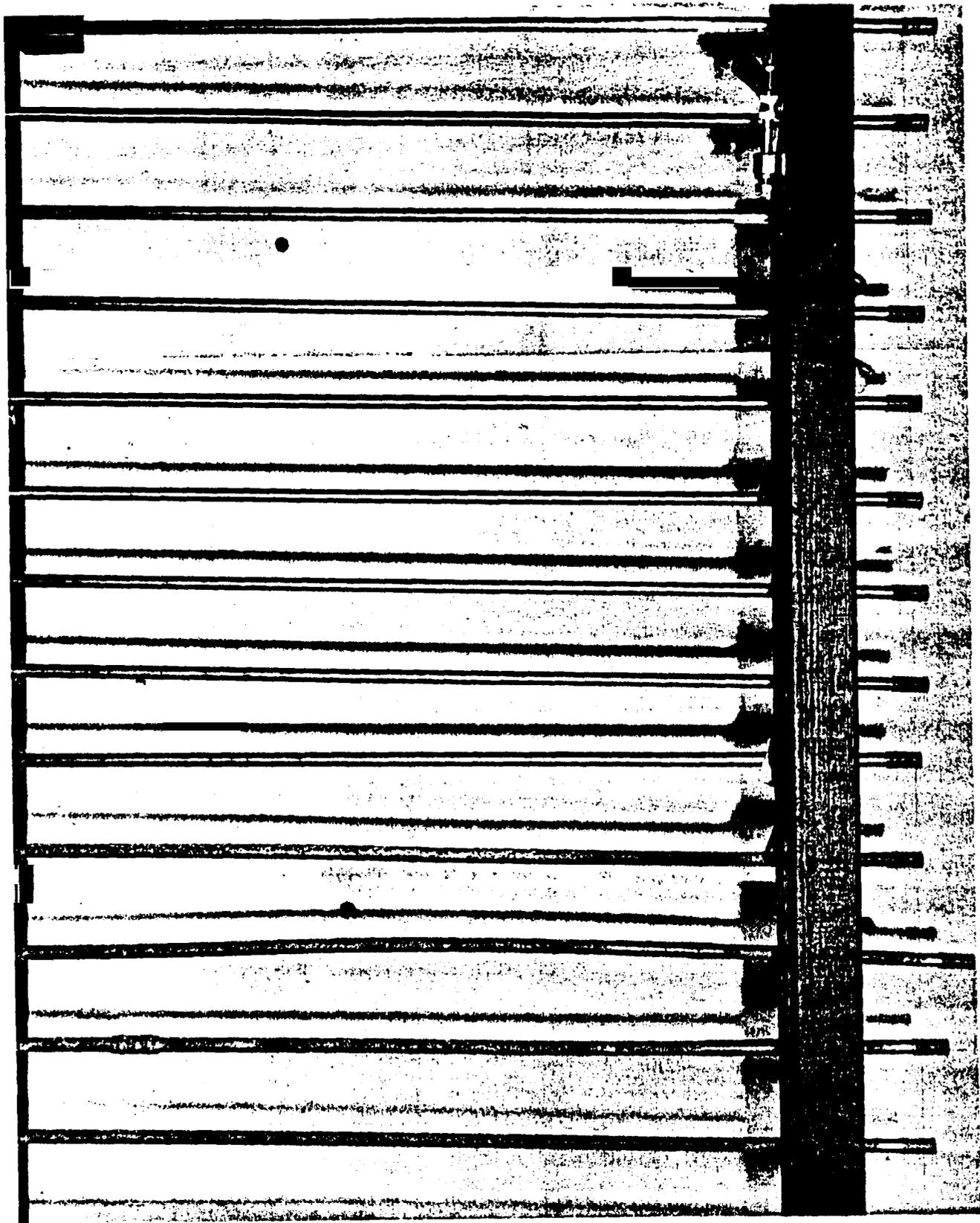


Figure 5. Tubing Samples in Sheltered Section of Rack Number 3 After 3-Months Exposure (The Four Organic-Zinc Coated Samples are Shown at Bottom>

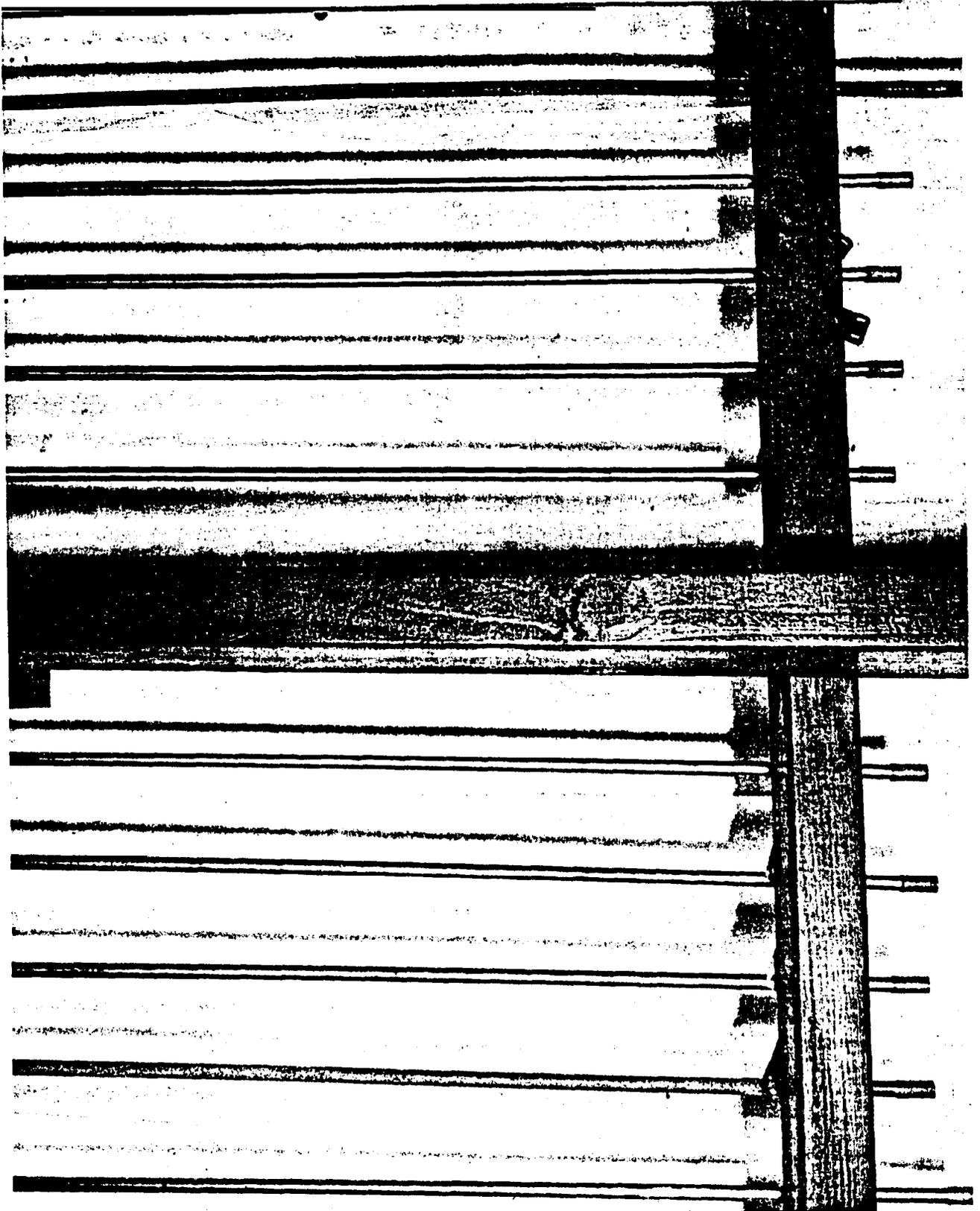


Figure 6. Tubing Samples in Sheltered Section of Rack Number 3 After 3-Months Exposure (The Inorganic-Zinc Coated Sample is Shown at Bottom)

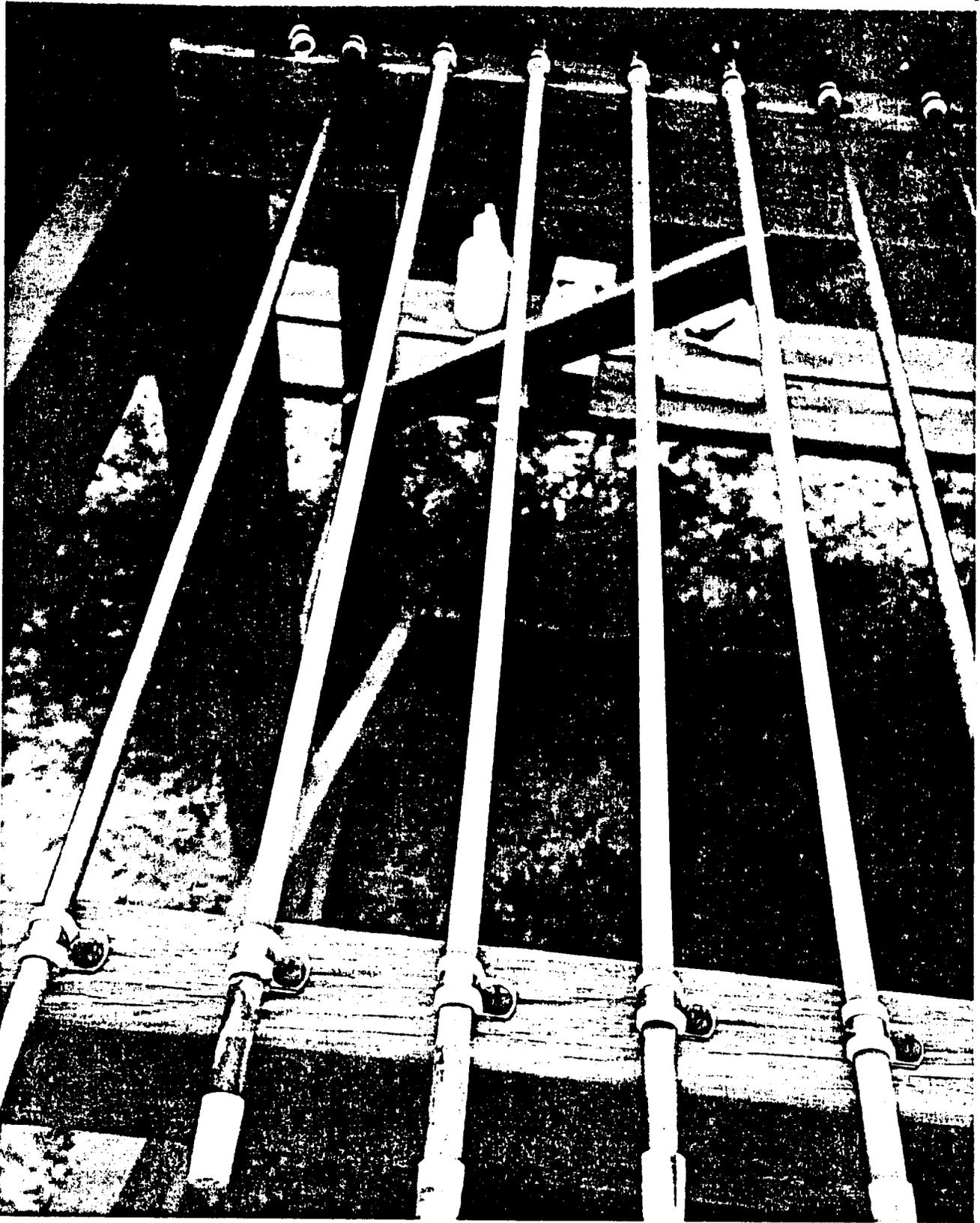


Figure 7. Bare and Organic-Zinc Coated Samples in Exposed Section of Rack Number 3 (After Approximately 30-Months Exposure)

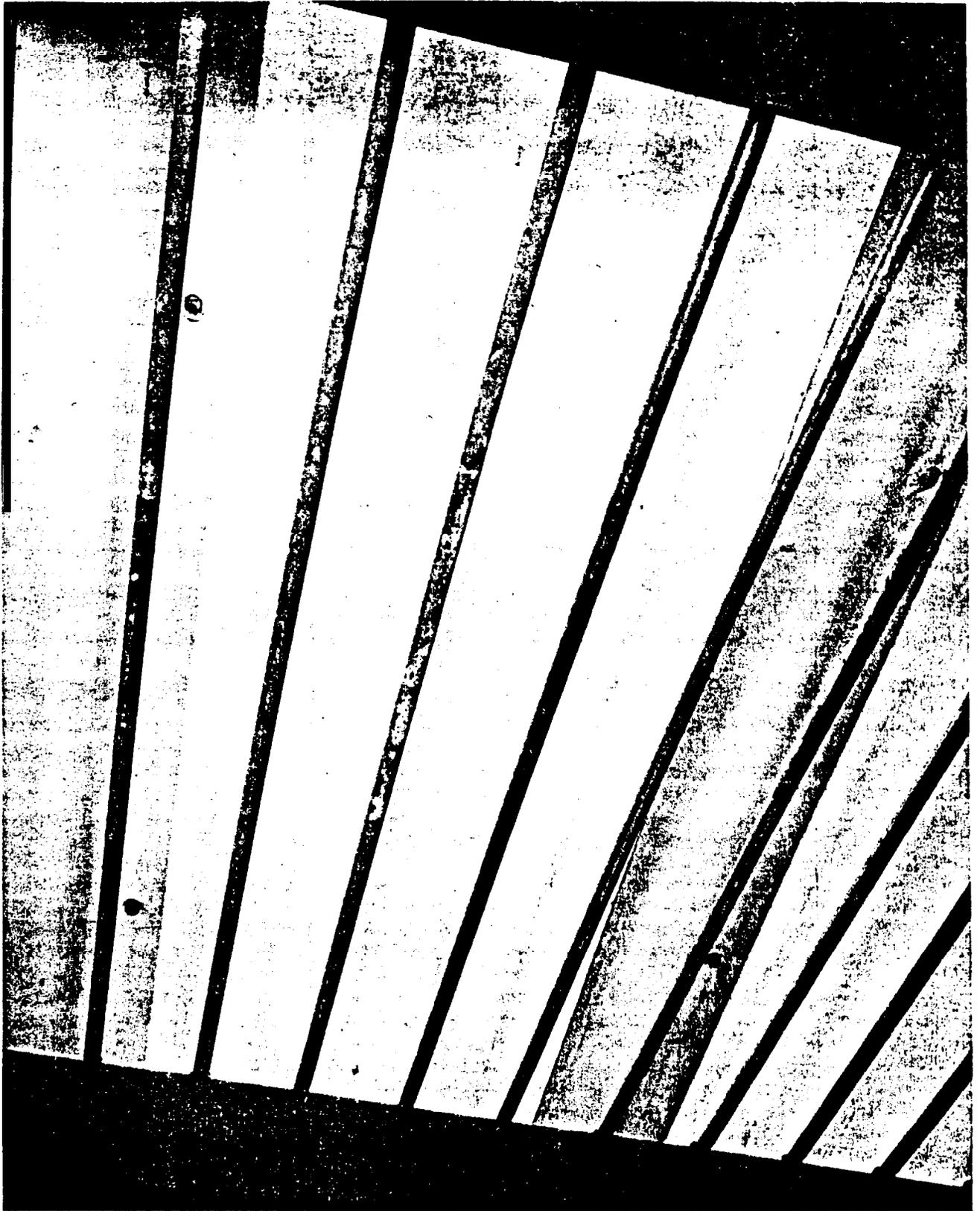


Figure 8. Bare and Organic-Zinc Coated Samples in Sheltered Section of Rack Number 3 (After Approximately 30-Months Exposure)

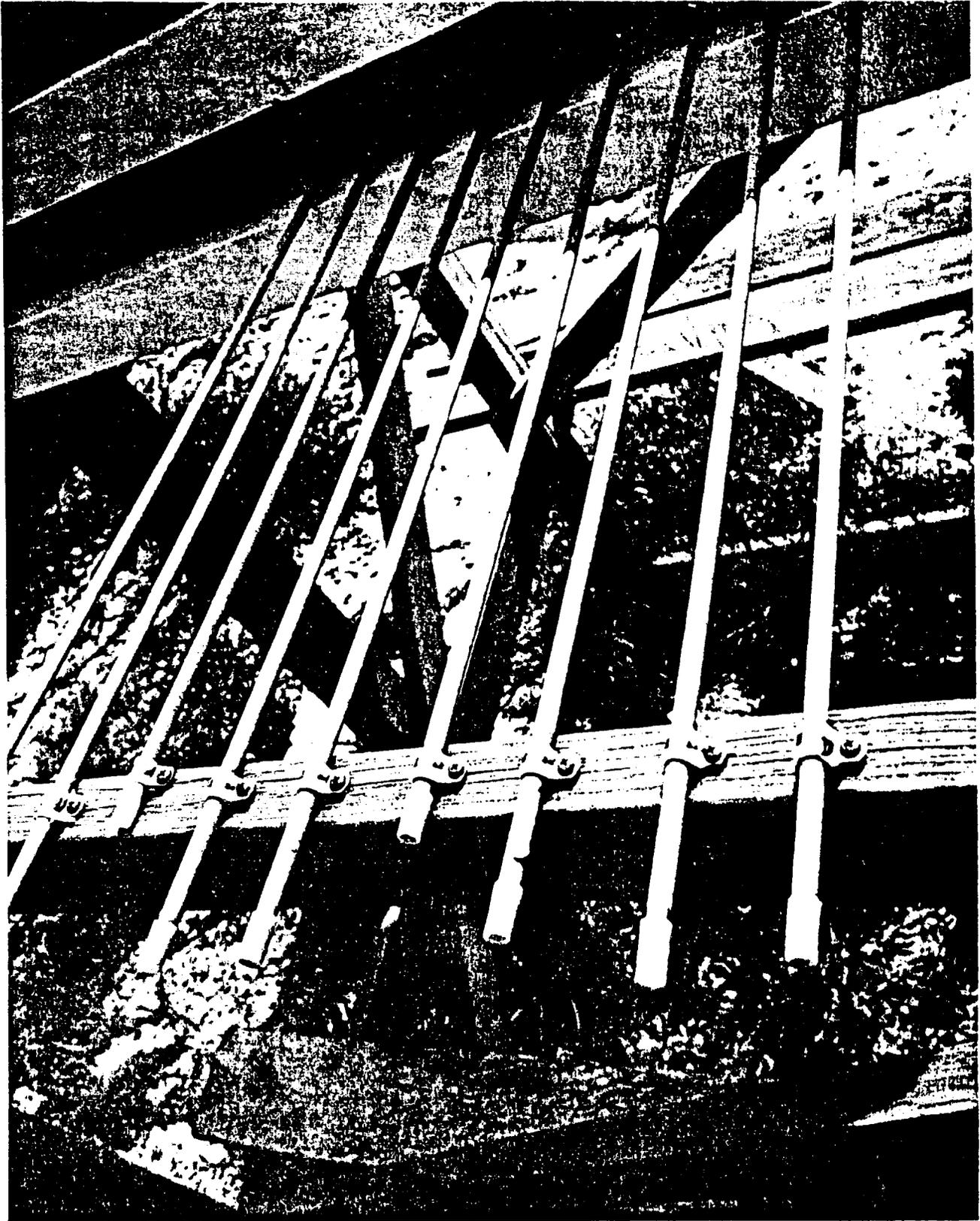


Figure 9. Coated Samples in Exposed Section of Rack Number 4 After 10-Months Exposure (2 Aluminum Filled Coatings & 1 Aluminum-Zinc Filled Coating, on Left; Remaining 6 Samples Organic Zinc Paint Coated)

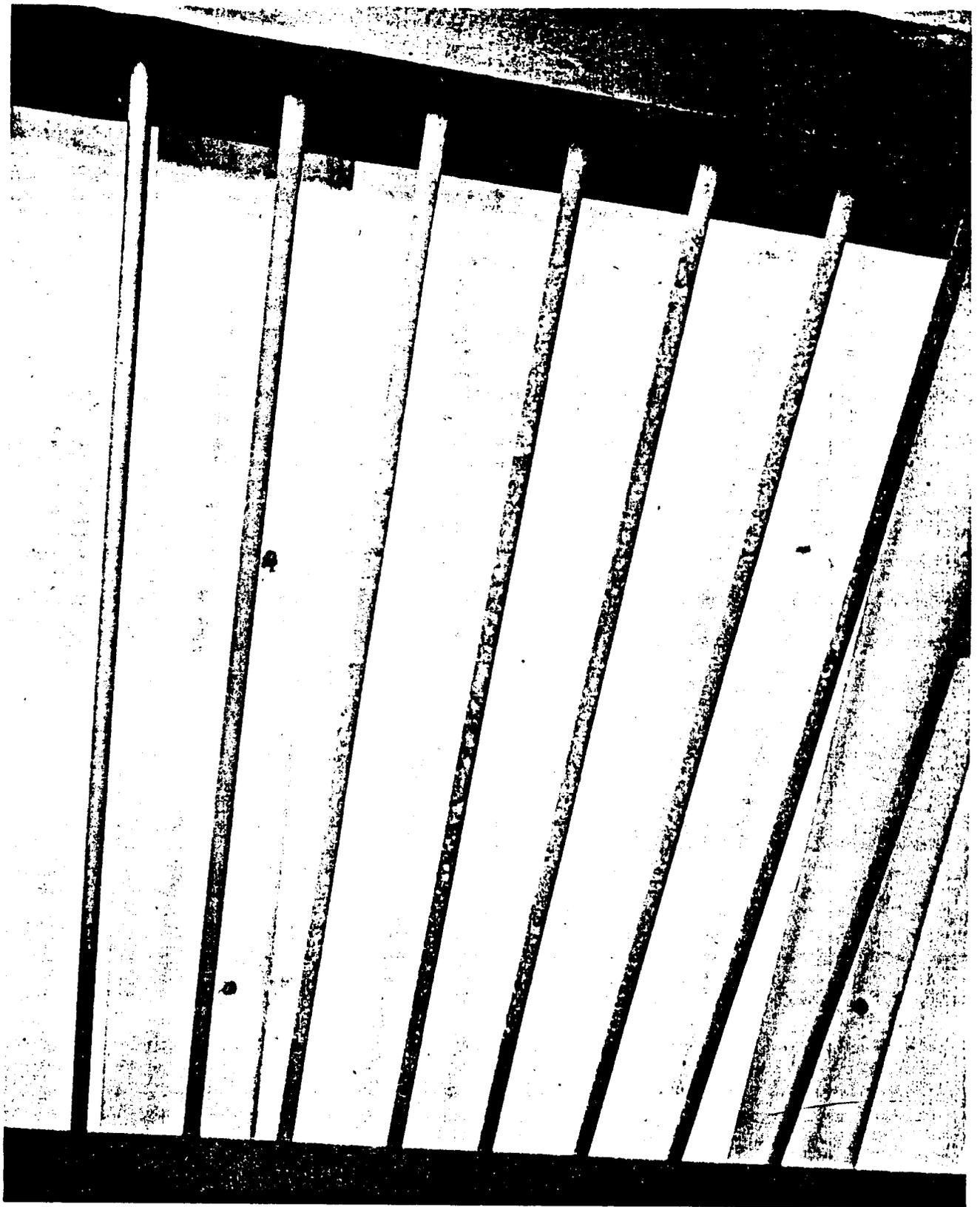


Figure 10. Coated Samples in Sheltered Section of Rack Number 4 After 10-Months Exposure (1 Aluminum Filled Coating & 1 Aluminum-Zinc Filled Coating on Left; Remaining 6 Samples Organic Zinc Paint Coated)

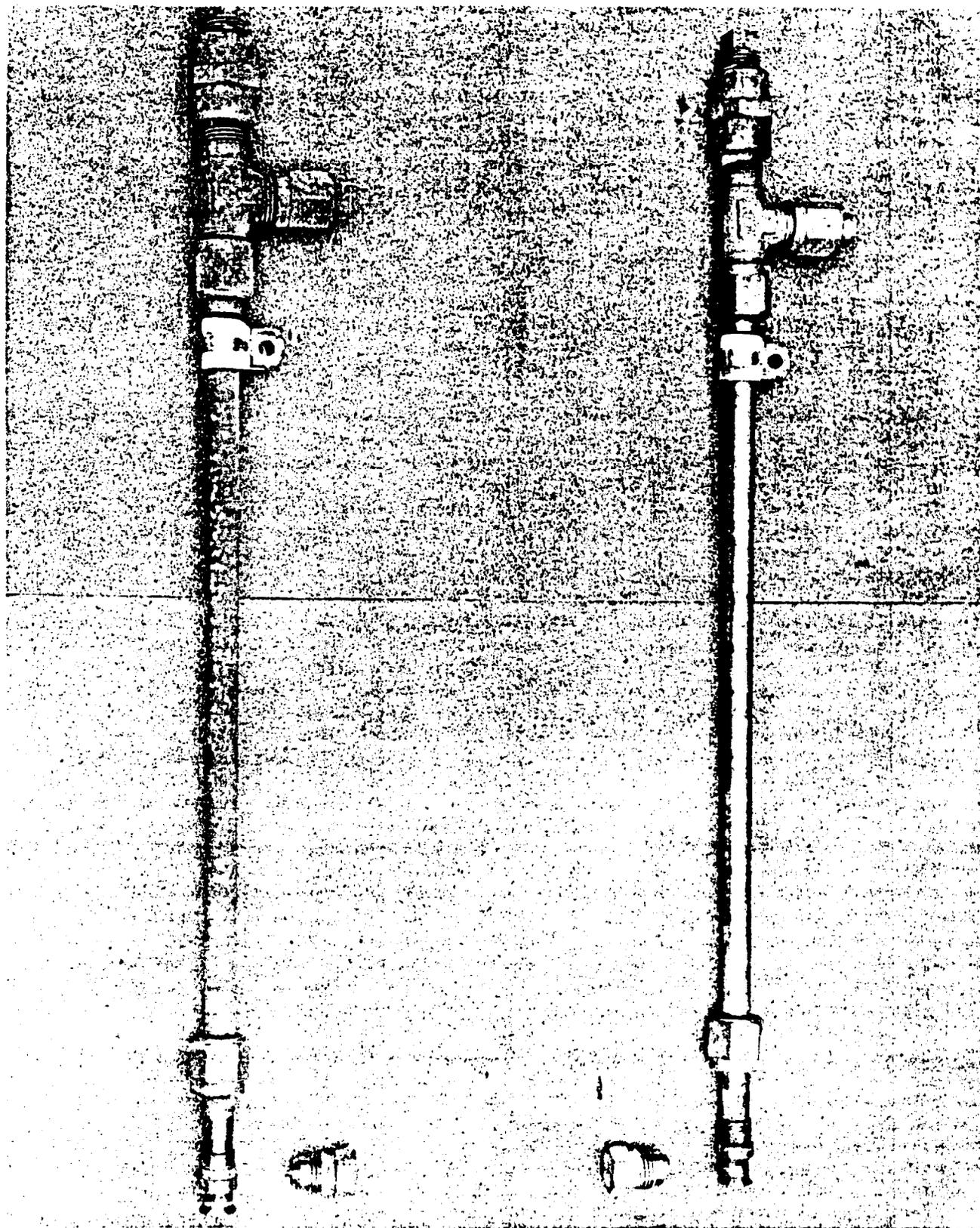


Figure 11. Coated & Bare Tubing Assemblies After 12 and 14 Months Exposure ,
Respectively, in the Sheltered Section of Rack Number 4
(Inorganic Zinc-Rich Paint Applied Over Sandblasted Surface)

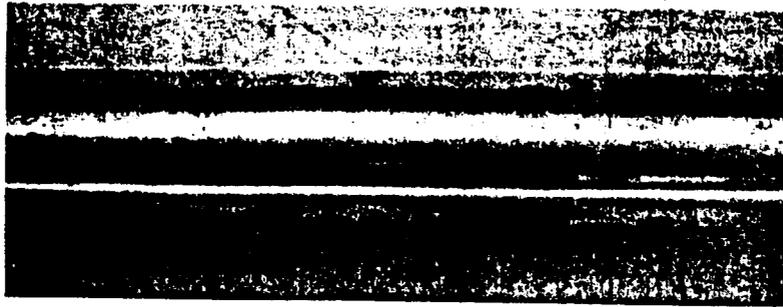
3.3 Metallurgical Analyses of Exposed Samples

3.3.1 This section of the report contains the results of the laboratory examinations performed on the exposure test samples removed from the test site in August and September, 1970, after a total exposure time of approximately 28 months. The following test materials are covered in this analysis:

<u>Sample Number</u>	<u>Material</u>
4	316 L
5	304L
6	347
7	304 1/8-Hard
8	316
9	321
10	304
37	316 (10MO 1734)

The portrayal of the results is done basically in the same manner for all of these test materials (which were bare tubing samples, and solvent cleaned prior to exposure). For each sample, photomicrographs of typical surface conditions in the exposed and sheltered sections are shown. A photomicrograph of the tubing cross-section in the area of deepest pit penetration found is also shown for each sample. The microsections were taken from the sheltered sections, and it is believed that deepest pitting for all materials occurred in these areas. Microscopic examination of the tubing surfaces so indicated. For comparative purposes, a similar analysis is presented for samples of bare Type 304L removed from Complex 34. It is known that perforation from pit penetrations occurred in some of the tubing, which prompted its removal from service. No perforations were found in the samples examined, and the pit cross-section shown is believed to be typical of the deeper pits. The results of this analysis are presented in Figures 12 through 21, and identified as follows:

<u>Figure</u>	<u>Sample Number</u>	<u>Material</u>
12	4	316 L
13	5	304 L
14	6	347
15	7	304 1/8-Hard
16	8	316 (ASTM-A269)
17	9	321
18	10	304
19	37	316 (10MO 1734)
20	LC-34	304L
21	LC-34	304L



VIEW A Magnification: 2X
Exposed Portion



VIEW B Magnification: 2X
Sheltered Portion



VIEW C Magnification: 80X
Cross-Section of Tubing Wall in Deepest Pit Area

Figure 12. Surface Characteristics and Pit Depth of Type 316L Exposure Sample



VIEW A

Exposed

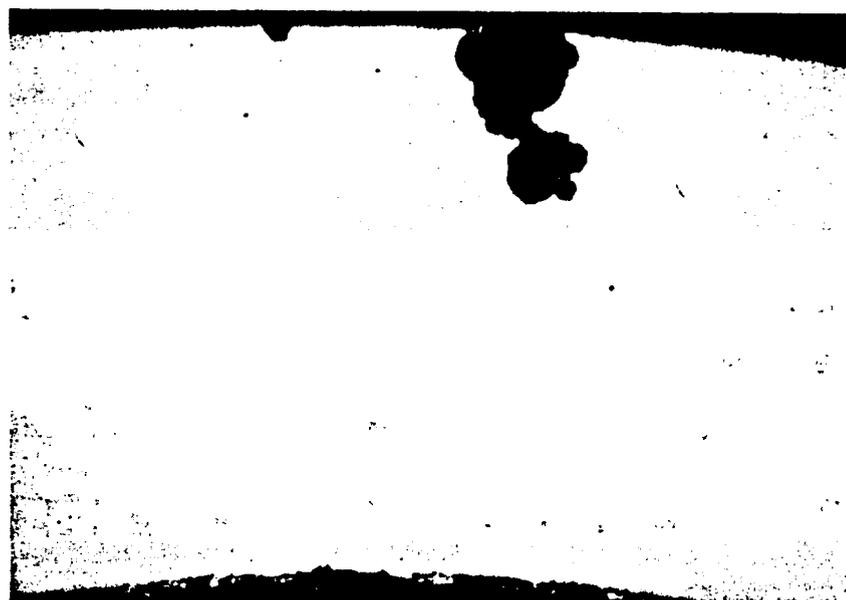
Magnification: 2X
Portion



VIEW B

Sheltered Portion

Magnification: 2X

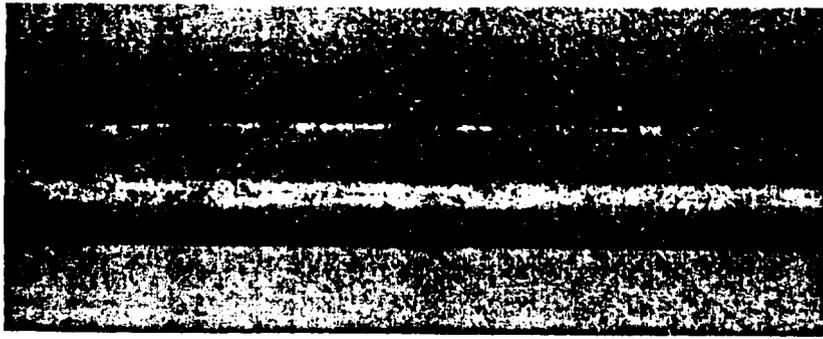


VIEW C

Cross-Section of Tubing Wall in Deepest Pit Area

Magnification: 80X

Figure 13. Surface Characteristics and Pit Depth of Type 304L Exposure Sample



VIEW A

Magnification: 2X

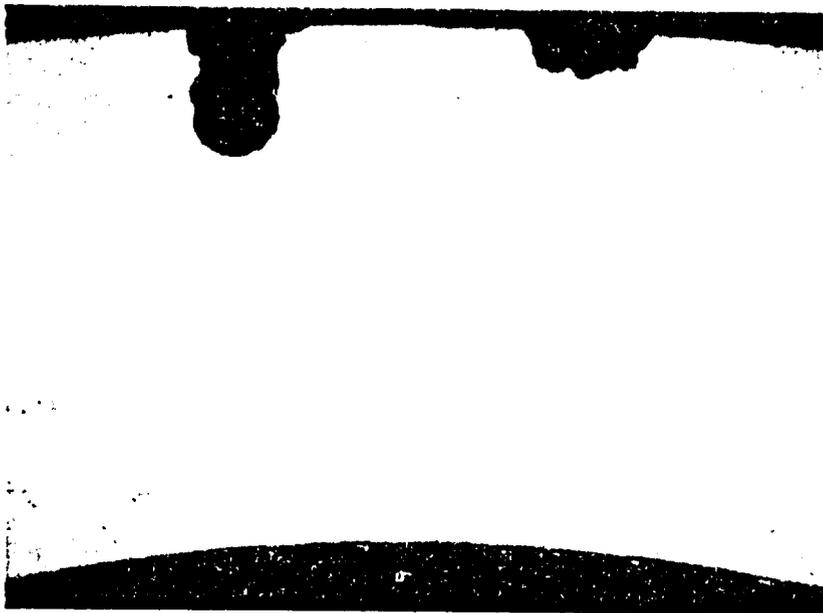
Exposed Portion



VIEW B

Magnification: 2X

Sheltered Portion



VIEW C

Magnification: 80X

Cross-Section of Tubing Wall in Deepest Pit Area

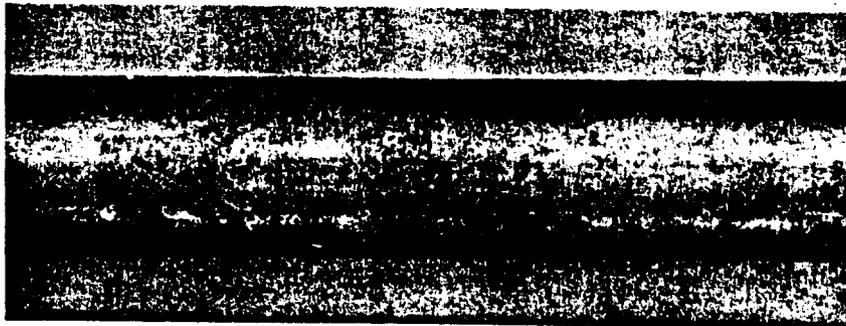
Figure 14. Surface Characteristics and Pit Depth of Type 347 Exposure Sample



VIEW A

Magnification: 2X

Exposed Portion



VIEW B

Magnification: 2X

Sheltered Portion

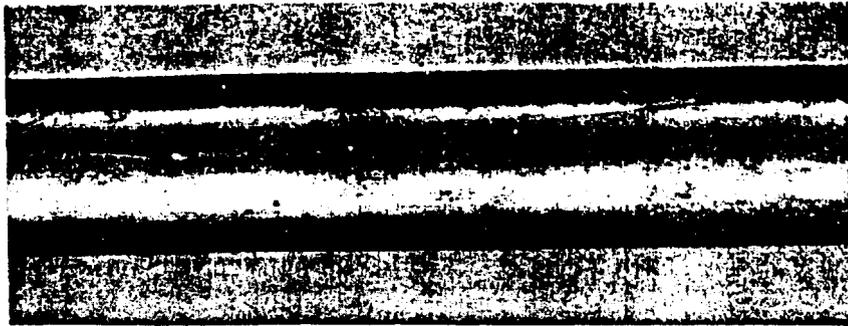


VIEW C

Magnification: 80X

Cross-Section of Tubing Wall in Deepest Pit Area

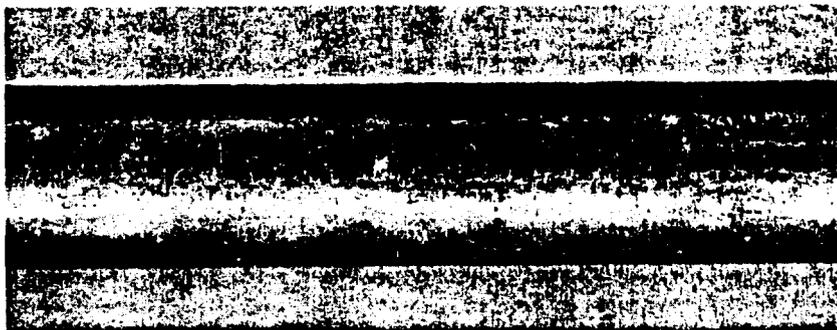
Figure 15. Surface Characteristics and Pit Depth of Type 304 1/8-Hard Exposure Sample



VIEW A

Magnification: 2X

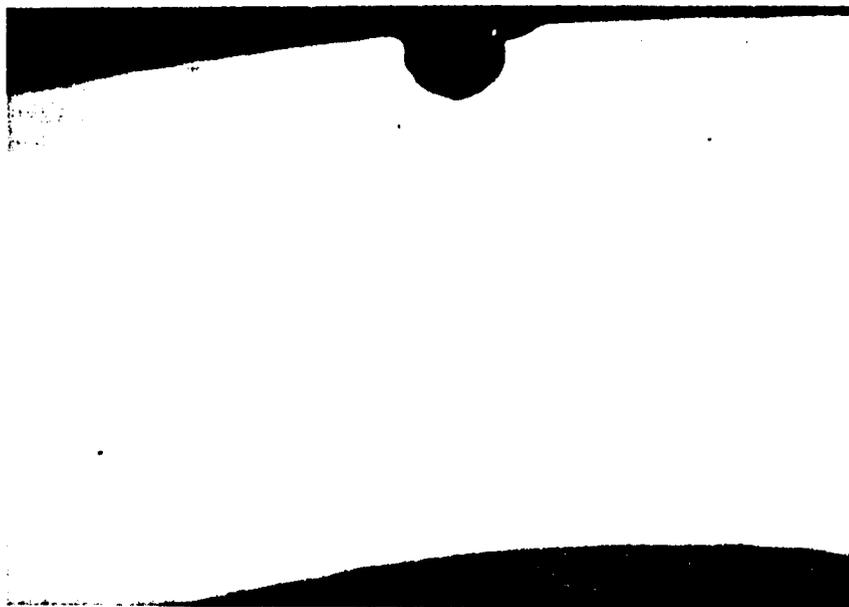
Exposed Portion



VIEW B

Magnification: 2X

Sheltered Portion

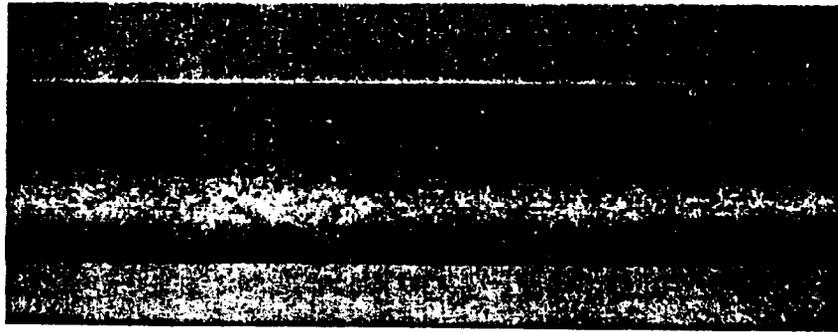


VIEW C

Magnification: 80X

Cross-Section of Tubing Wall in Deepest Pit Area

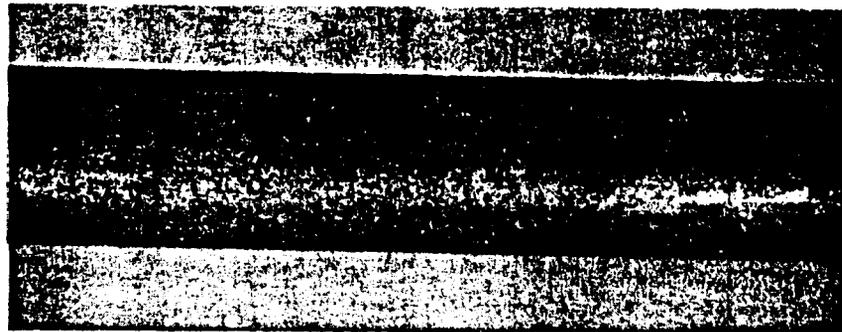
Figure 16. Surface Characteristics and Pit Depth of Type 316 (ASTM- A269) Exposure Sample



VIEW A

Magnification: 2X

Exposed Portion



VIEW B

Magnification: 2X

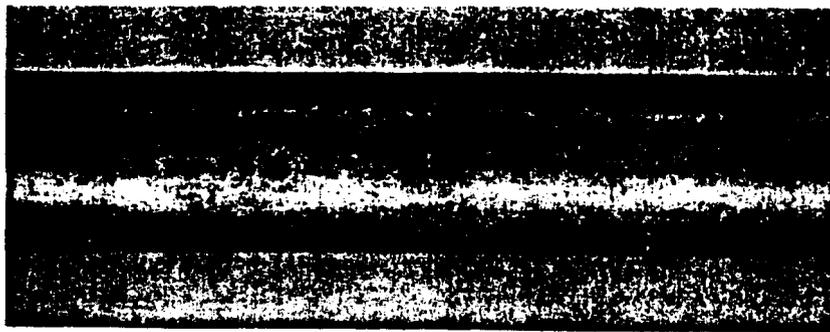
Sheltered Portion



VIEW C

Magnification: 80X

Figure 17. Surface Characteristics and Pit Depth of Type 321 Exposure Sample



VIEW A

Magnification: 2X

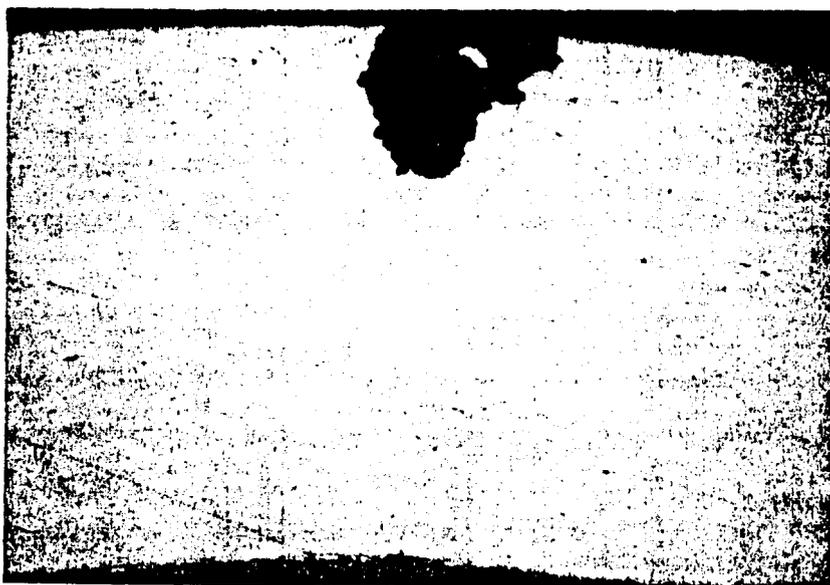
Exposed Portion



VIEW B

Magnification: 2X

Sheltered Portion



VIEW C

Magnification: 80X

Cross-Section of Tubing Wall in Deepest Pit Area

Figure 18. Surface Characteristics and Pit Depth of Type 304 Exposure Sample



VIEW A

Magnification: 2X

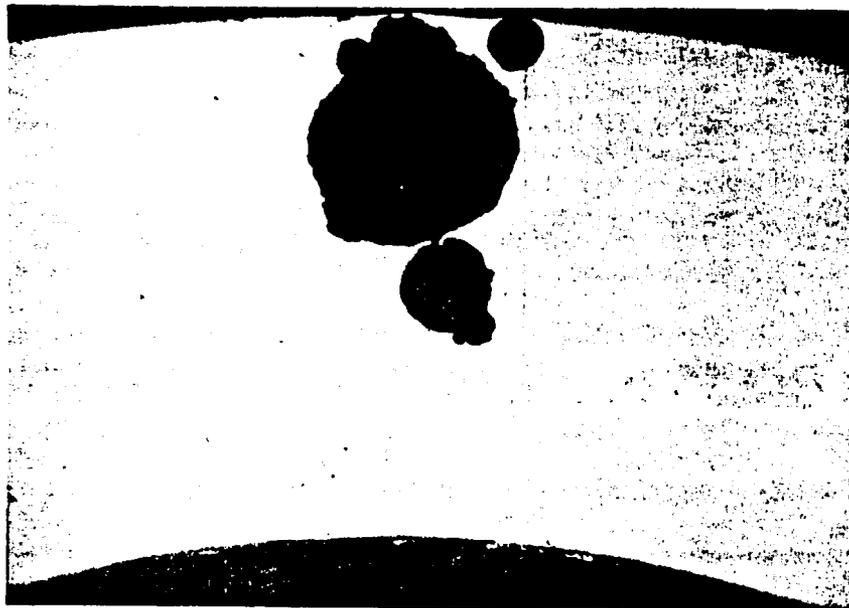
Exposed Portion



VIEW B

Magnification: 2X

Sheltered Portion



VIEW C

Magnification: 55X

Cross-Section of Tubing Wall in Deepest Pit Area
(Tubing Wall Thickness 0.049")

Figure 19. Surface Characteristics and Pit Depth of Type 316 (MSFC 10M01734) Exposure Sample. (Tubing Wall Thickness of Sample was 0.049")



VIEW A

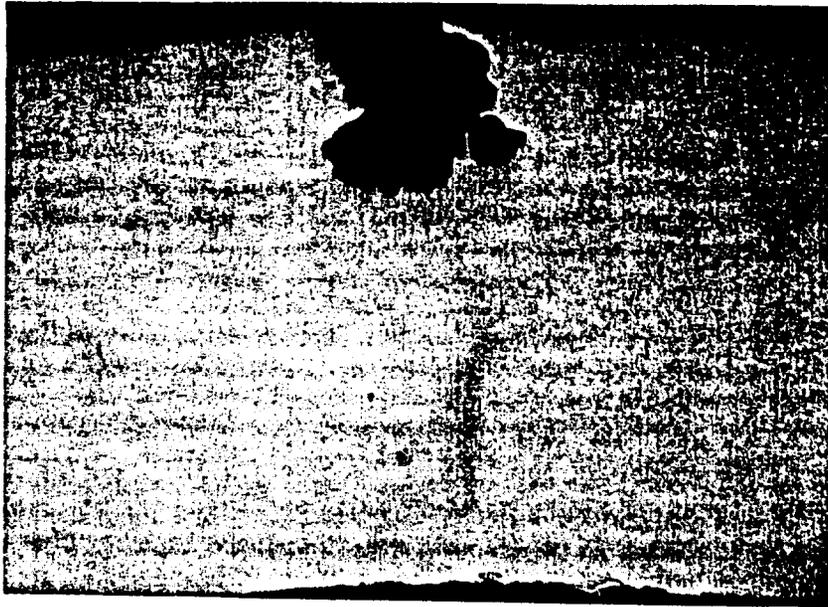
Magnification: 4X



VIEW B

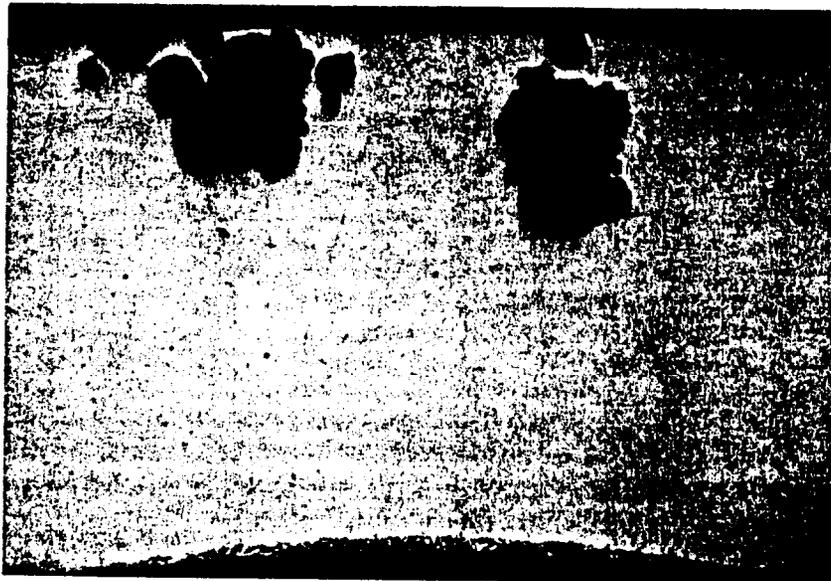
Magnification: 55X

Figure 20. Surface Characteristics of Pit Areas of Type 304L Tubing Removed From Complex 34



VIEW A

Magnification: 80X



VIEW B

Magnification: 80X

Figure 2 1. Cross-Sections Through Tubing Wall in Deepest Pit Areas, Type 304L Tubing Removed From Complex 34

3.3.2 The characteristic surface appearance of corrosion pits in austenitic stainless steels can be observed in the photomicrographs of the exposed portions of the tubing samples. The pit itself appears as a tiny dark spot in the approximate center of a small clear area, which is, in turn, surrounded by the usual reddish-brown deposit of corrosion products. This deposit is typically seen as a ring, or broad, generally circular band. These characteristics are usually obscured in the sheltered portion of the sample, because of the heavy accumulation of corrosion products. These heavy accumulations are prevented in the exposed portion by rain impingement.

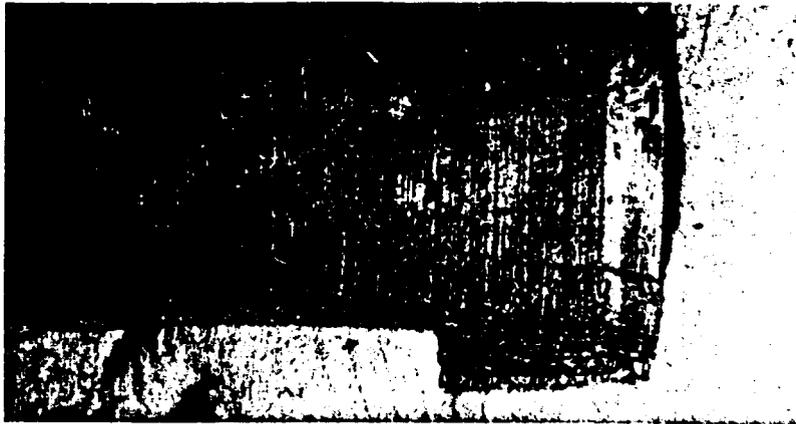
The photomicrographs of the tubing wall cross-sections show the depth of pitting for each material. These are believed to represent the deepest penetration existing in the test samples examined. However, because of the fortuitous nature of the pit population, and the limited techniques available for determining maximum depth of each and every pit, an exact comparative evaluation of "pitting rate" is not possible. It is evident that the pit morphology in the various test materials is basically similar, and is also similar to that in the samples obtained from service applications at KSC (e.g. Figures 1, 2, 20, and 21). There is clear evidence from the visual inspections that there is a much higher pit population in Types 321 and 347 than in Types 304 and 316. The Type 316 probably has the lowest pit population of all the grades tested. Obviously, the Type 316 does not, in contrast to a popular misconception have a lower pitting rate (rate of pit penetration into tubing wall) in actual service environments.

As a matter of fact, the deepest pits found to date in any of the samples have been in Type 316L and in the Type 316 (MSFC 10MO 17341, as is shown in Figures 12 and 19. This is not to suggest that Type 316 has a higher pitting rate than the other grades; in another Type 316 sample (Figure 16), no deep pits were found. The evidence cited here does suggest that no single austenitic stainless steel of the grades tested in this program is significantly better than the others for the fluid-systems applications in an environment of the KSC-type.

Further insight into pitting rate and the effects of service stresses from internal pressurization may be obtained from the pressurized test samples. It is possible that hoop stresses from internal pressurization can accelerate the pitting rate, and, if this is the case, a trend may be evident in the evaluation of the pressurized samples,

3.3.3 The most clearly evident effect of applied stresses on the structural integrity of the austenitic stainless steels in the fluid-systems applications is manifested in stress-corrosion failures, as mentioned previously. A failure of this type was discovered in the bare tubing assembly (Figure 11) that was removed from Rack Number 4 after 14-months of exposure at the beach test site. The B-nut sleeve had several longitudinal cracks, which apparently initiated on the inner tapered surface that was bearing against the tubing flare.

Figure 22 shows a photomicrograph of this inner surface, with the stress corrosion cracks and corrosion products, and a photomicrograph of a longitudinal microsection cut from the sleeve and prepared metallographically. In the photomicrograph, the branching nature of the stress-corrosion cracks can be seen. The small "stringers" in the microstructure are iron sulfide inclusions, which are typical of the Type 303 grade. Although the B-nuts and other major fittings used in the tubing assembly were the 316 grade (Type K), the B-nut sleeve (whose identity was not disclosed by markings) was Type 303, as was confirmed by chemical analysis. It is probable that Type 303 accounts for most of the stress-corrosion failures of tubing fittings that have occurred at KSC .



VIEW A

Magnification: 7X

Sleeve Inner Surface



VIEW B

Magnification: 80X

Longitudinal Microsection

Figure 22. Stress-Corrosion Cracking in Type 303 B-Nut Sleeve From Bare Tubing Assembly Removed From Rack Number 4 After 14-Months Exposure

4.0 DISCUSSION

4.1 Pitting Corrosion

For amplification of the previous references to the mechanisms of pitting corrosion, the following discussion is submitted. In pursuing these points, reference is made to the attached figures, which depict schematically the morphological and electrochemical conditions prevailing in the pitting corrosion of a section of stainless steel tubing. Figure 23 shows the tubing surface in the vicinity of an active 'pit, operating in a film of moisture in which there is a dissolved electrolyte. In the KSC area, this is usually sodium chloride, although various other compounds can serve as "solution-type" (ionic) conductors. Chloride ion, as pointed out by Fontana, has the apparently unique ability to penetrate the normally protective complex oxide layer on the stainless steel to cause pitting initiation. In the absence of the chloride ion, pitting is usually initiated at points where mechanical 'breakage of the oxide layer has occurred or at non-metallic inclusions present at the metal surface. Pitting, once initiated, usually continues whenever moisture is available (whether from condensation, salt fog, or other source). The center of the site, the pit itself, is the anode, within which are generated iron ions (ultimately Fe^{+++}) and hydrogen ions (H^+). At some distance away from the pit but in the moisture film is located the cathodic site which is a relatively large area of the unbroken oxide layer on the tubing surface. With this condition, there is a large driving force for enlargement of the pit, since the limiting factor in the electrochemical current generated by the cell is the area of the anode. The cell potential for the pitting of stainless steel is of the order of 0.7 volt. This type of electrochemical activity is called an "active-passive" cell. Hydroxide ions (OH^-) generated in the cathodic area surrounding the pit and ferric ions (Fe^{+++}) generated in the pit migrate toward the opposite electrodes and meet in a ring-shaped area around the pit. In this area, the brownish corrosion product, identified many times by x-ray diffraction analyses as consisting mainly of iron oxyhydroxide ($FeOOH$), is deposited on the stainless steel surface. Figure 24 shows the same basic pitting mechanism occurring in a cross-sectional view of the tubing wall. Note that hydrogen ions tend to accumulate within the pit itself, so that the pH may commonly be of the order of 1. The significance of this point has been re-emphasized recently in a technical note authored by B. F. Brown of the U.S. Naval Research Laboratory.¹ Brown notes the basic similarity of several forms of localized attack - stress-corrosion cracking, pitting, intergranular corrosion, crevice corrosion, etc. - with respect to the acid condition at the site of the corrosion attack. The acid is formed by hydrolysis of the

1. B. F. Brown, "Technical Note: Concept of the Occluded Corrosion Cell," Corrosion, Vol. 26, No. 8, August 1970, pp. 249, 250.

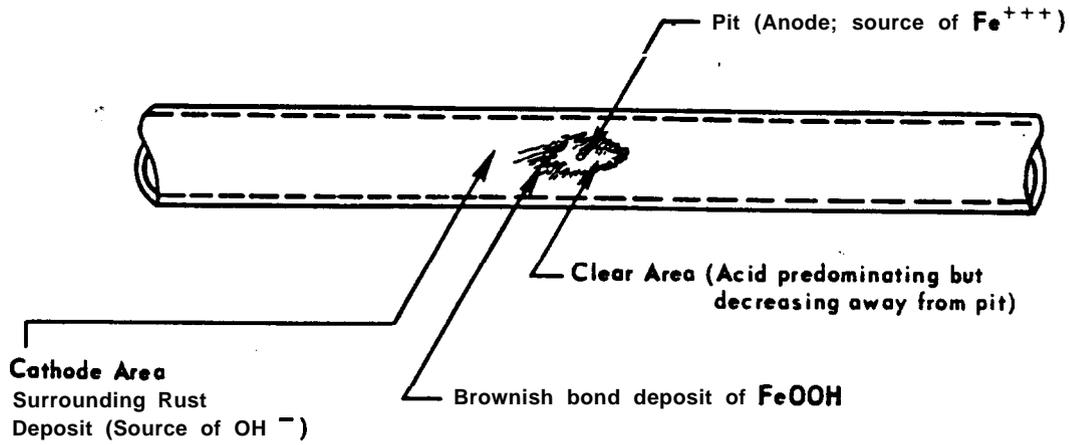


Figure 23. Surface of Tubing in Pit Area

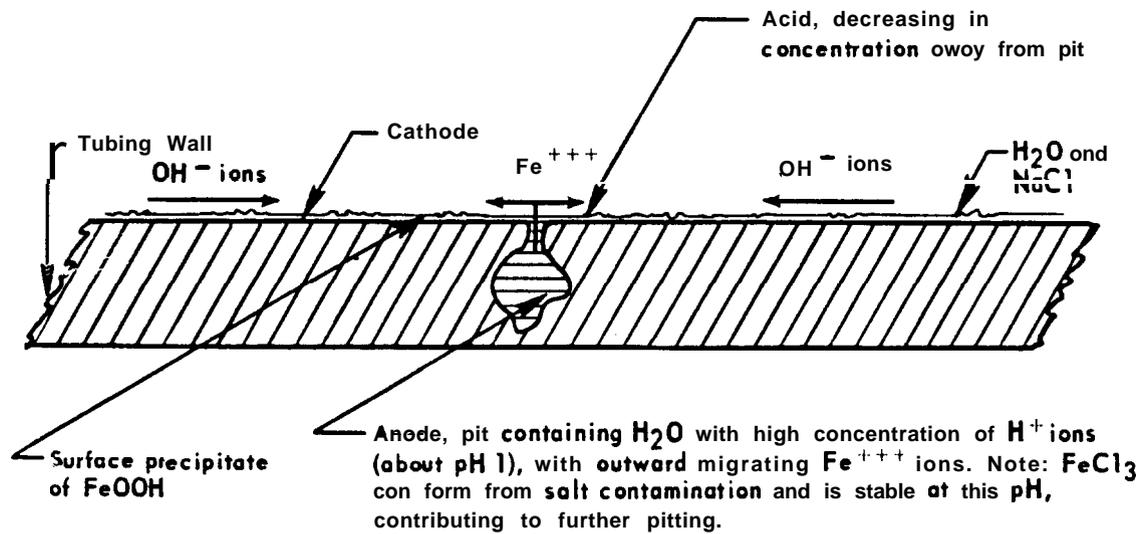


Figure 24. Longitudinal Section Through Tubing Wall in Pit Area

electrolyte, and it persists and accumulates mainly because of the local site geometry, which tends to limit interchange of the corrosion cell constituents with the bulk environment. These two factors lead to a highly stable and insidious "metal dissolver." Brown remarks on the high degree of acidity attained in the occluded cells - recently determined to be pH 2 or less, a factor which is apparently not widely recognized. This characteristic was clearly demonstrated during the recent examination, in the KSC Materials Testing Branch, of the B-nut sleeve shown in Figure 22. During examination of the cracked areas with a low power microscope, bubbling of liquid retained within one of the larger cracks was observed. This activity was occurring about 10 days after the sample had been removed from the corrosion test site and brought to the laboratory. Some of the liquid was absorbed into a piece of pH-sensitive paper (Hydrion Paper), with which the pH of a test solution is indicated by color change. The pH of the "stress-corrosion liquor" was determined by this means, to be in the range of 1.5 to 2.0. Similar activity undoubtedly occurs in corrosion pits, particularly those that have grown to larger size within tubing walls. Corrosion activity can continue in these sites even after the parts have been removed from the primary corrosive environment. For example, pitting of some of the stainless steel tubing lines on one of the mobile launchers moved from the pad to a bay in the VAB could continue to be active there as long as sufficient moisture was present in the atmosphere to prevent drying of the pits.

4.2 Stress-Corrosion Cracking

The exact mechanisms associated with stress-corrosion cracking in austenitic stainless steels are still being mooted by the authorities. It seems probable, however, that in the annealed materials stresses in excess of the yield strength are required to initiate stress-corrosion cracking. In other words, crack initiation occurs in material undergoing plastic deformation. Pronounced stress concentrations can result in local plastic zones in a part that is generally stressed below yield strength. This circumstance probably occurs on the bearing face of B-nut sleeves, that is, where they bear against the back surface of tubing flares. Corrosion pits can also result in sufficient stress concentrations to produce plastic zones. Similar conditions obtain in parts of all tubing fittings used in the assembly of stainless steel tubing lines. When these plastic zones are accessible to a corrosion environment, particularly one containing chloride ion, stress-corrosion cracking is a distinct possibility. Many of these fittings still in use at KSC have been fabricated from one of the grades of Type 303 stainless steel, 303 or 303 Se (one containing 0.15 percent sulfur and the other containing 0.15 percent selenium). These elements are added to the alloy to improve machinability, particularly of small parts that are produced on screw-machines. The improved machinability of the 303

alloy over that of type 304 or 316 is well established. However, from the service environment aspect, the 303 grades are metallurgical abominations. The iron sulfides or iron selenides constitute sites for ready access of the environment at the surface, and provide a preferred cracking path for stress corrosion through the bulk of the material. The complete elimination of the 303 alloy for KSC applications should result in improved reliability of tubing fittings.

5.0 CONCLUSIONS

The following tentative conclusions are drawn, based on the work performed to date.

- 5.1 Pitting corrosion, basically identical to that observed in service applications of austenitic stainless steel tubing lines at KSC, has been observed to initiate in tubing samples of Type, 304, 304L, 316, 316L, 321, and 347 within 11 days in beach exposure tests.
- 5.2 Surface treatments, such as electropolishing and chemical passivation, delayed corrosion initiation but did not prevent its occurrence after 30 days exposure.
- 5.3 Corrosion pits have grown, in some of the tubing test samples, to a depth of about 65 percent of the wall thickness in 28 months of exposure.
- 5.4 There appears to be a significant difference in pitting-depth rate, with some of the Type 316 samples showing the highest rate. However, this occurrence is believed to be fortuitous (without statistical significance) because of the highly localized aspect of the pitting mechanism. It is probable that no single alloy, among those evaluated, is distinctly better than any other with regard to the penetration rate of individual pits.
- 5.5 Stress-corrosion cracking of Type 303 B-nut sleeves occurred after 14 months exposure of tubing assemblies at the beach corrosion test site.
- 5.6 Pitting corrosion has been prevented in the austenitic stainless steels for a period of at least 28 months by the application of zinc-rich coatings (both organic and inorganic-base). Stress-corrosion cracking has been prevented in tubing fittings for a period of at least 12 months by application of inorganic-base zinc-rich coatings.
- 5.7 An aluminum-rich organic base coating, now in the development stages, appears very promising for application to stainless steel tubing, fittings, and flex sections, in the prevention of pitting and stress-corrosion cracking.

APPENDIX A

List of Failure Analysis Reports Covering Pitting Corrosion Failures of Stainless Steel Tubing Lines and Bellows Sections and Stress Corrosion Failures of Tubing Fittings.

Part 1: Pitting Corrosion

<u>MAB Report No.</u>	<u>Date</u>	<u>Subject</u>
1411-66	2 November 1966	Malfunction Investigation: Leaks in Stainless Steel GO2 Manifold, Astronauts' Trailer.
779-67	7 June 1967	Malfunction Investigation: Pitting of Stainless Steel Tubing.
1427-67	16 October 1967	Failure Analysis of. Stainless Steel Tubing from Complex 37.
2032-67	1 February 1968	Failure Analysis of Type 304 Stainless Steel Tubing, 75M 14636-12.
267-68	6 March 1968	Failure Analysis of Stainless Steel Tubing from the Transporter Leveling System.
398-68	27 March 1968	Failure Analysis of Convolute Flexible Hose from LH ₂ Storage Vent Line.
426-68	24 April 1968	Failure Analysis of Stainless Steel Tubing, AS 205, LC-34.
623-68	30 April 1968	Failure Analysis of Pitted and Cracked Stainless Steel Tubing.
668-68	6 May 1968	Failure Analysis, Leaking of Stainless Steel Tubing in GH2 Line.
702-68	4 June 1968	Failure Analysis of Stainless Steel Tubing.
800-68	24 June 1968	Failure Analysis of a Bellows, 75M0 2515, Swing Arm Hydraulic System, Complex 34.

APPENDIX A (Continued)

<u>MAB Report No.</u>	<u>Date</u>	<u>Subject</u>
1029-68	22 July 1968	Failure Analysis of Stainless Steel Bellows, Spacecraft Piping System.
047-69	21 February 19 69	Failure Analysis of Flexible Hose, P/N 75M0 10284-23C from Service Arm #4 on LC-39
133-69	17 May 1969	Metallurgical Inspection of Flexible Hoses,
216-69	26 June 1969	Failure Analysis of Nitrogen Tetroxide Fill Line, P/N 32LM-55MJ60G.
283-69	28 August 1969	Failure Analysis of Four-Inch Diameter Flexible Hose, P/N 75M17761, S/N 5285010, LOX Vaporizer System A430, Complex 37.
077-70	2 April 1970	Failure Analysis of Flexible Hose, P/N 32LM-55MJ60G, S/N 26122, Used to Supply N ₂ O ₄ to LM Main Propulsion System.
229-70	24 November 1970	Failure Analysis of 1/4-Inch Tube Assembly, P/N 65824147-7, from the 3000 PSI GN2 Line, S-IC Forward Umbilical Service Unit.

Part 2: Stress-Corrosion Cracking

951-67	5 July 1967	Malfunction Investigation: Cracking of AN Quick-Disconnect Fittings, LC-37B.
1160-67	28 August 1967	Malfunction Investigation: Cracking of B-Nut Sleeves in GN 2 Lines.
1393-67	12 October 1967	Failure Analysis, Cracking of B-Nut Sleeves Used in Tube Assembly, Service Arm #8, Complex 39.

APPENDIX A (Continued)

<u>MAB Report No.</u>	<u>Date</u>	<u>Subject</u>
065/066-69	25 February 1969	Failure Analysis of B-Nut Sleeves, S-II 4GSE.
066-70	3 April 1970	Failure Analysis of Flared Tubing Sleeves (2) MC 12564 and (1) MC 12506, from Pneumatic and Hydraulic Tubing Assemblies on Service Arms of Mobile Launcher No. 3.
189-70	25 September 1970	Failure Analysis of Tubing Assemblies, Including Unions, Sleeves, B-Nuts, and Tubing, from the Pneumatic Distribution Systems, ML-2 and ML-3.

APPENDIX B

Literature Survey of Corrosion and Corrosion Protection of Stainless Steels.

1.0 INTRODUCTION

The purpose of this literature survey is to review and assess the available recent literature dealing with corrosion mechanisms, corrosion testing in sea coast environments, and the protective paint type coating systems. The first part of the report covers the literature on corrosion and corrosion testing of stainless steels. The second part of the report covers the literature on anti-corrosion coatings for stainless steels. The literature references used in the preparation of this report are included in the Bibliography.

2.0 CORROSION OF STAINLESS STEELS

2.1 This portion of the report is a review of pertinent references obtained in a search of Chemical Abstracts, for the period January, 1950 through December 1967, and Corrosion Abstracts from 1961 through 1967. Key words used in searching the Chemical Abstracts Indexes were "pitting corrosion" and "stress corrosion" with references pertaining to the **austenitic** stainless steels noted. In this search, three hundred and six abstracts were examined, and about twenty-five of these appeared to be of sufficient value to warrant examination of the entire articles. Of these twenty-five, several articles in foreign language journals were not obtained because of the time required to obtain translations.

2.2 Approximately 1,000 abstracts were reviewed in Corrosion Abstracts, covering the following categories: On-Location Tests, Forms of Local Cell Attack, Marine Atmospheric Environment, Metallic Coatings, **Non-Metallic Coatings**, Multiple Metallic-Nonmetallic Coatings, Ferrous Metals and Alloys, and Valves, Piping, and Meters. Twenty-one articles were selected, but of these, ten were **not readily** available, or were available only in foreign language.

2.3 This part of the report is subdivided into two sections, the first reviewing the literature on pitting corrosion and exposure testing and the second on stress-corrosion cracking.

2.3.1 Pitting Corrosion and Exposure Testing

2.3.1.1 The articles of most relevance to this study are probably those dealing with the mechanisms of pitting

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corrosion in stainless steels and the effects of environment and compositional variables on the resistance to pitting corrosion. A particularly lucid elementary treatment of the subject is that by Robinson (1)¹. As explained by Robinson, when a metal undergoes uniform corrosion, it is possible to make a reasonable prediction of the life of the metallic component provided that a rate of corrosion has been established for this material in prior tests. The corrosion rate is determined by exposure of a sample to the corrosive environment and the measurement of the weight loss or of uniform penetration of the material. However, with some metals and alloys, the corrosive attack is confined to small, discrete areas on the metal surface, resulting in very localized corrosion of an otherwise unaffected material. Pitting is the extreme example of the latter type of corrosion, and it is particularly insidious since perforation of a part may occur before there is obvious evidence of corrosive processes. This sort of corrosion is most frequently encountered with "passive" alloys (e.g., aluminum and stainless steel), which rely for their corrosion resistance on a surface protective film. Robinson's paper describes the initiation of a pit by perforation of the passive oxide film. This initial step is usually associated with the presence of chloride or sulfate ions, which move through "weak points" in the film and enlarge them to expose the anodic active site. An active-passive electrochemical cell is established with the anode being the pit site and the cathode being the surrounding film-covered area. The corrosion products, instead of precipitating in direct contact with the active metal surface (which condition would tend to suppress further corrosion), are deposited where the outbound metal ions (from anodic dissolution of the metal) and the inbound hydroxyl ions from the electrolyte meet. This is often seen as a small ring of iron oxide deposited around the pit area.

¹Numbers in parentheses refer to the Bibliography appended.

APPENDIX B (Continued)

2.3.1.2 Two papers by Greene and Fontana (2, 3) describe experiments on the basic electrochemical mechanisms involved in the pitting corrosion of stainless steels. These investigators employed an ingenious "artificial pit," consisting of a fine wire anode and a thin sheet cathode one inch square. The electrodes were placed in a flask, which contained the electrolyte and in which the atmosphere and dissolved gases could be controlled through gas inlet tubes. Pit initiation and growth was observed with the electrodes short-circuited or with controlled potentials applied. In experiments with Type 304 stainless steel in a ferric chloride electrolyte, pitting was usually initiated immediately upon short-circuiting the cell. Pit growth was characterized by a very erratic corrosion rate, as indicated by current flow, during this early growth period. This initial instability of the corrosion pits was considered by Greene and Fontana to be an indication of the autocatalytic nature of the pitting process. The stability of the "artificial" pits increased with time, and loss of pit activity during the later stages of growth was rarely observed. Pit growth was characterized by an increase in corrosion rate with time and no limiting corrosion rate was observed in the duration of the experiments. The effects of several variables on pit growth were determined with the "artificial pit" and are described below. Agitation of the electrolyte (ferric chloride) slightly increased the activity of growing pits. The atmosphere within the test cell produced no observable effect on the pitting tendencies with ferric chloride as the electrolyte. With Type 304 stainless steels, 0.1 molar solutions of ferric bromide and cupric chloride produced pit growth similar to that of 0.1 molar ferric chloride. Tests with Type 316 stainless steel showed that pitting corrosion was not sustained with ferric chloride concentrations below 0.3 molar. In further studies with the "artificial pit" (3), Greene and Fontana showed, by polarization measurements, that the autocatalytic nature of pitting could be attributed to self-stimulating electrochemical changes at both anode and cathode areas

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- 2.3.1.3 A paper by Schwenk (4) describes studies to determine in what potential range pitting will occur in austenitic stainless steels, the kinetics of pitting, and what materials will inhibit pitting. Of particular interest was the observation that with a Type 316 stainless steel pitting occurs with sodium chloride electrolytes in concentrations as low as 0 .-1 molar. Schwenk found that as pitting corrosion proceeds to the point that a large number of active pits exist (and a relatively large total anode area is involved), a "repassivating" effect occurs. Also, growth of pits in irregular shapes is attributed to partial repassivation of active areas. The repassivating effect was found to be dependent on molybdenum content (increasing with increased molybdenum).
- 2.3.1.4 Recent studies of the pitting potential in stainless steels are described in papers by Hospodaruk and Petrocelli (5) and Leckie and Uhlig (6). In the former paper, the authors described tests to determine the pitting potentials of several stainless steels in nearly neutral chloride solutions. Most of the prior work had been done with acid electrolytes. The experiments by Hospodaruk and Petrocelli showed that the nucleation of pits on an otherwise passive surface is a function of the electrode potential. For a given chloride ion concentration and alloy composition, pitting does not occur until a certain potential is reached or exceeded. This pitting potential is characteristic of the alloy and may be used as a measure of the relative pitting tendency of various alloys. According to these authors, the mechanism by which chloride ion effects the initial breakdown of the passive film at certain sites is still in question and is presently being explored.
- 2.3.1.5 The Leckie and Uhlig paper also affirms the existence of a critical potential for pitting in stainless steels. The ability of certain ions, such as nitrate, to inhibit pitting of stainless steels in ferric chloride solutions is explained as resulting from a shift in the potential to a more noble value when the

APPENDIX B (Continued)

nitrate ion is present. Based on their experiments, these authors postulate a mechanism for destruction of the passive film on stainless steels as follows: at a sufficiently high surface concentration of chloride ions, oxygen in the passive film is displaced locally by chloride ions. At these points, the anodic overvoltage for dissolution of the stainless alloy is considerably reduced wherever the metal is in contact with chloride ion compared to metal in contact with the oxygen, and hence metal ions rapidly enter solution resulting in a pit.

- 2.3.1.6 Greene and Judd(7) have investigated the relation between dissolution kinetics and resistance to pitting corrosion in materials including 304L and 316 stainless steel. They have shown that the ratio of dissolution rates in the presence and absence of chloride ion is inversely related to pitting resistance. In a paper by Tomashov, Chernova and Markova (8) an investigation of the influence of alloying elements on the resistance of 18 Cr-14 Ni steel to pitting corrosion is reported. Molybdenum, silicon, and vanadium showed the greatest influence on corrosion resistance. Resistance to pitting was greatly increased at 5 percent concentrations. Additions of those elements caused the pit sites to shift from the grain surface near the boundaries to the grain boundaries.
- 2.3.1.7 The effects of alloy composition on pitting tendencies of austenitic stainless steels were also described in an excellent paper by Streicher (9). Streicher's experiments were performed with several "standard" steels, such as Types 302, 304, 304L, 316, 316L, 321, and 347, and some modified alloys - 302B (containing 2.50 percent silicon), a silicon-modified 316, and several alloys with high nitrogen content. The pitting tendencies in chloride solutions were evaluated for these alloys in two conditions: (a) pickled (to reduce the effectiveness of the oxide coating) and (b) pickled and passivated. These experiments revealed that the

APPENDIX B (Continued)

pitting tendency of Type 316 and Type 304 in the pickled condition was essentially the same but the passivation treatment decreased pit initiation for all of the alloys. The response of Type 316 to passivation is much greater than that of Type 304, which is attributed to the effect of molybdenum in re-establishing the passive film, while decreasing the carbon content decreased pit initiation. Steels containing higher amounts of nitrogen showed less pitting than those containing normal amounts but no effect on pitting was associated with the presence of stabilizing elements such as columbium in Type 347 and titanium in Type 321.

- 2.3.1.8 A different approach to the problem of pitting corrosion, concentrating on the physical and chemical characteristics of the protective film, was discussed in an early paper by Rhodin (10). Rhodin's findings indicate that the film properties are particularly sensitive to alloy composition, corrosive medium, and surface treatments. These properties reflect the intrinsic capacity of a metal surface to protect itself against corrosion. A specific example is that of a silicon-modified Type 3161, whose superior resistance to pitting corrosion was correlated with a mutual passive film enrichment in silicon and molybdenum and corresponding film depletion in iron.
- 2.3.1.9 A paper by Alexander, Southwell, and Forgeson (11) describes exposure tests performed in the Panama Canal Zone on several stainless steels. The effects of several environments such as inland, lake water immersion, seashore, sea water mean tide, and complete sea water immersion were determined. Significant pitting was obtained only in partial or complete immersion in sea water. In these tests frequency of pitting was less in Type 316 than in Types 302 and 321. On the basis of depth of pitting, however, there was little difference noted among these three alloys. K. G. Compton (12) discusses briefly the effects of location, local

APPENDIX B (Continued)

topography, humidity, temperature, rain, and atmospheric contamination on the exposure of test specimens to marine atmosphere.

2.3.2 Stress-Corrosion Cracking

2.3.2.1 The occurrence of transgranular stress-corrosion cracking in austenitic stainless steels in service applications stimulated considerable research activity on the subject in recent years. Since most of these service failures involved high-temperature applications such as steam piping, etc., the testing methods applied in these investigations have involved relatively high temperatures. Papers by Staehle, Beck, and Fontana (13), Thomas, Ferrari, and Allio (14), and Leu and Helle (15), describe tests in hot, aqueous chloride solutions of varying chloride concentrations used to evaluate the susceptibility of various alloys to stress-corrosion cracking. It was shown in these papers that, at temperatures of 400° F, Type 304 stainless steel can undergo cracking at applied stresses as low as 2,000 psi and chloride concentrations as low as 50 parts per million. While tests such as these do not of course represent service conditions involved in our subject applications, they do yield useful information on the relative susceptibility of different alloys and different metallurgical conditions of a given alloy. Papers by Uhlig and Lincoln (16) and Hawkes, Beck, and Fontana (17) show that cold work generally increases the susceptibility to cracking, with the most severe effect being associated with about 10 percent reduction by cold work. In the Hawkes, Beck, and Fontana paper, differences in resistance of Types 304, 309, and 316 to stress corrosion cracking were reported to be minor.

2.3.2.2 Different results relative to the effects of alloy content on stress corrosion were reported in papers by Bamartt, Stickler and van Rooyen (18) and Stickler and Barnartt (19). These investigators

APPENDIX B (Continued)

found that, in a more highly alloyed base steel (16 percent chromium, 20 percent nickel), additions of molybdenum up to 1.5 percent or titanium up to 0.5 percent increased the tendency to stress-corrosion cracking. It was postulated that the mechanism by which this occurs is similar to that proposed by Forty - a "restricted-slip" cracking mechanism (20). According to this theory, when a crack is formed within the surface layer it will propagate into the underlying metal only if dislocation movement is highly restricted. Propagation ceases if the crack enters a "soft" region, such as a pre-existing slip band. Therefore, alloys that readily cross slip should be resistant to this type of cracking. Characteristically, alloys that readily cross slip have comparatively high stacking-fault energies. Generally speaking, the stacking fault energies of the austenitic stainless steels are relatively low and, hence, cross slip is restricted. According to the papers previously cited, additions of molybdenum and titanium further lower the stacking fault energies, thus further reducing the opportunities for cross slip. The experimental data cited by these authors tends to confirm this theory.

3.0 ANTI-CORROSION COATINGS

- 3.1 This part of the report presents the results of a search conducted in Chemical Abstracts for the period 1948 through February 1968, using the following terms as descriptors:

- 3.1.1 Coatings - stainless priming.
- 3.1.2 Enamels - Enameling of, - stainless.
- 3.1.3 Lacquers - Lacquering of, - stainless.
- 3.1.4 Paints - Painting of, - stainless.
- 3.1.5 Finishes - Finishing, - stainless.
- 3.1.6 Steel, Stainless - coating.

APPENDIX B (Continued)

3.1.7 Steel, Stainless - corrosion.

3.1.8 Steel, Stainless - painting.

3.1.9 Steel, Stainless - priming.

3.2 Nine references were found to have some relevance to the subject study. Of these nine, four relate generally to surface preparation prior to painting or to the application of fired enamel coatings. These articles were not considered to be of significant practical importance to this program. The remaining five items were abstracts of patents. These are presented in bibliographic form below.

3.2.1 Coating of Stainless Steel with Chromates for Salt Spray Corrosion Resistance

Chromating of stainless steel to improve its resistance to salt-spray corrosion (U.S. patent 2,991,205 4 July 1961). The corrosion resistance of stainless steel of all types--in industrial atmospheres or salt spray is improved by chromating, as with Zn or Cd. The finish can then be restored by polishing or buffing without detriment to the corrosion resistance. The preferred CrO_3 bath and coating conditions are the same as applied to ordinary steel (U. S . patent 2,768,104, 23 October 1956) but no preliminary surface treatment other than cleaning is required. Chromate coatings weighing 40 mg/sq ft were applied to bright-finished Type 430 stainless steel strip by immersion in an aqueous solution containing 2 percent CrO_3 and 0.66 percent sugar at 70° F, and Erichsen cups were formed from coated and uncoated specimens and tested in a 20 percent NaCl spray. Uncoated specimens rusted in 48 hours, buffed specimens in 72, coated in 165, and buffed and coated specimens did not rust in 600 hours.

3.2.2 Coating of Stainless Steel with Organic Esters of Ti or Zr

Method of coating the surface with transparent film and the product resulting therefrom (U.S. patent 2,768,909, 30 October 1956). A transparent flexible film is comprised of hydrolysis products of organic esters of a metal containing Ti or Zr, such as butyl titanate, ethyl titanate, etc. An ethyl titanate solution comprising 1.0 percent by weight of the ester,

APPENDIX B (Continued)

the balance ethanol was prepared by dissolving titanate at room temperature in the solvent. The solution thus obtained was sprayed onto a stainless steel sheet and was then air-dried for 40 hours, relative humidity approximately 50 percent. A thin, clear, transparent film resulted, which was extremely hard and adherent to the steel and could not be removed therefrom even by rubbing with a solvent soaked rag.

NOTE: No mention made in Chemical Abstracts of this system's corrosion resistance.

3.2.3 Coating of Stainless Steel with Oxalates

"Activation of oxalate metal-coating compositions" by R . C. Gibson to Parker Rust Proof Company (U .S . patent 2,617,749, 11 November 1952).

An active oxalate solution for the protective coating of austenitic stainless steel during mechanical work involving extensive plastic deformation, which is used along with a soap lubricant, aqueous oxalic acid, ferric ion, and 1.5 - 40 percent thiocyanate ion. In the preferred practice, the oxalic acid is in excess of that required to form ferric oxalate, the ferric ion is 0.4 to 6 percent and the thiocyanate ion is 1.5 to 20 percent. When ferrous oxalate is used in preparing the solution, H_2O_2 is added to oxidize Fe^{++} to Fe^{+++} . The coating is formed on the steel by immersion in the solution for 3 - 15 minutes and may be enhanced by dipping in a slurry of hydrated lime.

NOTE: There was no mention of field service corrosion protection afforded by this coating.

3.2.4 Coating of Steel (Stainless) with black, abrasion resistant coats

Black-coating stainless steel by H. W. Cobb to Armco Steel Corporation (U .S . patent 2,542,994, 27 February 1951).

Adherent, flexible, abrasion-resistant black coatings are produced on stainless steel by first immersing the steel in a molten bath of $Na_2Cr_2O_7$ and/or $K_2Cr_2O_7$. Then, the coated metal

APPENDIX B (Continued)

is subjected to an electrolytic cathodizing treatment in a fused dichromate bath for 5 - 10 minutes at a current density of .05 - 4.0 amps/in². A stainless steel anode is used. The temperature of the fused salt baths is maintained at 320-400° for Na₂Cr₂O₇ or 400-500° for the mixed salts. The stainless steel is cleaned by the customary methods before the blackening treatment.

NOTE: There was no mention of field service corrosion protection afforded by this coating.

3.2.5 Coating on Stainless Steel, from hydroxy compound polymer reaction DIC and TMP p. 17739a, 64, January June 1966

Hardened copolymers containing hydroxyl groups based on acrylates by G. Louis to Badische Anilin- and Soda - Fabrick, A. G. (German 1,201,556, 23 September 1965).

This article describes specific compounds that react and form copolymers which may be spread on stainless steel forming a nontacky film on standing at room temperature for 2 hours.

NOTE: Again, there was no reference to the degree of corrosion protection that might be afforded.

4.0 CONCLUSIONS

-4.1 From this review of the accessible literature, the following conclusions appear warranted:

- 4.1.1 Data from reported exposure tests in sea coast environments have very limited applicability in the subject study. These have generally failed to reveal the serious degree of corrosion experienced in the KSC area.
- 4.1.2 Theoretical studies indicate a superiority in the passive surface film of steel compositions containing molybdenum (e.g., Type 316). Such films are more resistant to penetration and undergo repassivation more readily than steels with lower molybdenum compositions (e.g., Type 304). These considerations are consistent with test data, which show a lower pitting frequency for Type 316 than for Type 304 but little difference

APPENDIX B (Continued)

in depth of pitting between the two alloys. Evidently, once the passive film is penetrated, the active-passive cell corrosion mechanism operates at virtually the same rate for all compositions of the austenitic stainless steels. A beneficial effect on the passive film was also obtained with experimental steels of unusually high silicon content.

- 4.1.3 Stress-corrosion cracking, which is a serious problem with tube fittings of certain compositions in the KSC area, is not known to be of serious concern in stainless steel tubing. However, data from the literature indicate a probable susceptibility of partially cold-worked material in chloride environment. There was also some indication that molybdenum may increase the tendency for stress-corrosion cracking in hot chloride environments, and a mechanism for this was proposed (**restricted-slip mechanism**). Whether this mechanism can operate at ordinary temperatures in an atmospheric chloride environment has not been established.
- 4.1.4 The patent literature describes several coating systems designed for application to stainless steels. Corrosion test data were presented for only one of these, a zinc or cadmium chromate. A beneficial effect on corrosion resistance (by the salt-spray test) was produced by the application of this coating.

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